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PART I

by

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ABSTRACT

Sampling and analysis was designed to determine ambient concentrations of ethylene dibromide and other brominated chemicals near production facilities in El Dorado and Magnolia, AK. A characterization was made of the environmental matrices - air, water, soil, sediment and biota - for the presence and levels of ethylene dibromide, vinyl bromide and other related chemicals surrounding the bromine industry.

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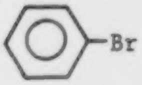
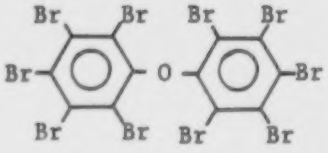
NAMES, ABBREVIATIONS, AND STRUCTURAL FORMULAS OF BROMINATED COMPOUNDS

Methyl Bromide (MB)	CH_3Br
Vinyl Bromide (VB)	$CH_2{=}CH\text{-}Br$
Bromoform (BF)	$CHBr_3$
Bromoethane (BE)	$CH_3CH_2\text{-}Br$
1,2-Dibromoethane (EDB)	$Br\text{-}CH_2CH_2\text{-}Br$
1-Chloro-2-bromoethane (CBE)	$ClCH_2CH_2\text{-}Br$
Allyl Bromide (AB)	$CH_2{=}CH\text{-}CH_2\text{-}Br$
1-Chloro-3-bromopropane (CBP)	$Cl\text{-}CH_2CH_2CH_2\text{-}Br$
1-Chloro-2,3-dibromopropane (DBCP)	$Cl\text{-}CH_2CHBrCH_2\text{-}Br$

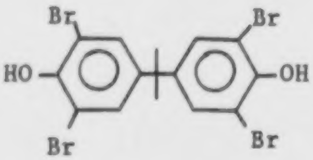
Bromobenzene (BB)



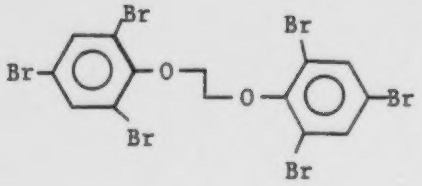
Decabromobiphenyl ether (Decabrom)
syn.-decabromobiphenyl oxide



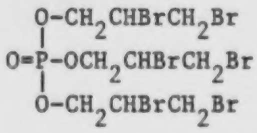
2,2'-Bis(dibromo-4-hydroxyphenyl)propane
(Tetrabrom)
trivial name - Tetrabromobisphenol A



1,2-Bis(2,4,6-tribromophenoxy)ethane
trade name - Firemaster 680®



Tris-(2,3-dibromopropyl)phosphate (TRIS)
trade name - Firemaster LVT23P®



$$\begin{array}{l} \quad O\text{-}CH_2CHBrCH_2Br \\ O{=}P\text{-}OCH_2CHBrCH_2Br \\ \quad O\text{-}CH_2CHBrCH_2Br \end{array}$$

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1.0 SUMMARY AND CONCLUSIONS

Development and/or validation of methods for the collection and analysis of brominated chemicals (inorganic and organic) in environmental samples - air, water, soil, sediment, and biota - was conducted and these techniques were applied to the characterization of the environment surrounding the bromine industry in El Dorado and Magnolia, AK. The final analytical protocols which were adopted in this research program are given in Appendix A.

Evaluation of a miniature impinger train for the collection of halides and halogens indicated that if molecular chlorine and bromide ion were present in air the displacement of bromide from the first impinger would occur. Thus, false high values of molecular bromine would be observed. Determination of chloride and bromide was conducted by turbidimetric measurements; the detection limit was approximately 10 $\mu g/m^3$. Differentiation of chloride and bromide ions was accomplished by ion-exchange techniques or, in some cases, the bromide was detected by a fluorescence quench method using fluorescein. Inorganic fluoride was directly determined using a fluoride ion-specific electrode and the detection limit was ~2 $\mu g/m^3$.

Collection of volatile brominated organics in ambient air utilized Tenax GC® and carbon sorbents. In some cases aluminum vacuum cannisters were used as alternatives to the sorbent methods for obtaining methyl chloride, methyl bromide, vinyl chloride and vinyl bromide. Airborne particulates were trapped on glass fiber and cellulose filters. Methods for recoverying of brominated organics from air particulates, water, soil, sediment and biota were developed and/or validated. Techniques such as inert gas purging or solvent extraction were used to isolate the brominated materials from the condensed phases.

The principal method for the identification of brominated organics was gas chromatography/mass spectrometry/computer (gc/ms/comp). Quantitation was performed by gc/ms/comp and gc/ec. Alternate detection methods such as neutron activation, spectrophotometry, and scanning electron microscopy/X-ray dispersion were used for exploration and confirmation of the presence of brominated substances.

A total of 26 brominated organic compounds was identified in environmental samples collected from a geographical area associated with the bromine industry (Table 1.1). Many of the chemicals were detected in environmental matrices off plant property indicating that their transport into the neighboring environment was occurring. Quantification of most of the chemicals in various environmental media (Table 1.1) was also conducted.

Examples of selected results exhibitng highest concentrations observed in environmental samples are given in Tables 1.2 and 1.3. These preliminary results indicate a spatial spreading of brominated compounds into the environment.

Additional research would be required to establish the extent of environmental contamination and man's exposure and body burden.

Table 1.1. HALOGENATED AND OTHER CHEMICALS IDENTIFIED IN THE ENVIRONMENT

Substance	Matrix
chlorodibromopropane	air
1-chloro-2,3-dibromopropane	air, water, soil, sediment, front and tail brine
1,2-dibromoethane	air, water, soil, sediment
difluorodibromomethane	air
methyl bromide	air
bromobenzene	air, soil, sediment
bromoethane	air
bromoform	air, sediment, front and tail brine
1-chloro-2-bromoethane	air, water, sediment
1-chloro-3-bromopropane	air
1,3-dichloropropane	air
vinyl bromide	air
bromodichloromethane	air, tail and front brine
allyl bromide	air
1 or 2-bromopropane	air
bromopropene	air, water
chlorobromopropene	air
1,1-dibromo-2-chloropropane	air
dibromopropane	air
dibromoethene	water
chlorobutene	water

(continued)

Table 1.1 (cont'd)

Substance	Matrix
bromodichloropropane	water
1,2-dichloroethane	water, soil, sediment
trichloroethylene	water
Decabrom®	air particulate, soil, sediment, human hair
Tetrabromobisphenol A	air particulate, soil, sediment, human hair
Tris	air particulate, soil
Firemaster 680®	air particulate, soil
dibromochloromethane	front and tail brine
styrene	air
benzene	front and tail brine
toluene	front and tail brine
dimethyldisulfide	front and tail brine
thiacyclopentane	front and tail (?) brine
dithiol propane isomer	front and tail brine
ethylbenzene	front brine
_n_-undecane	front and tail brine
_n_-dodecane	front and tail brine

Table 1.2. MAXIMUM CONCENTRATIONS OF BROMINATED CHEMICALS OBSERVED IN SELECTED ENVIRONMENTAL SAMPLES

Company/Community	Chemical	Medium	Quantity
Great Lakes Chemical Corp.	Cl_2/Br_2	Air	183,000 ng/m^3
	Cl^-/Br^-	Air	876,000 ng/m^3
	EDB	Air	271,283 ng/m^3
	Decabrom	Air	94,118 ng/m^3
	Decabrom	Soil	>>225,000 μg/Kg
Velsicol Inc.	Cl^-/Br^-	Air	91,000 ng/m^3
	Cl_2/Br_2	Air	158,000 ng/m^3
	EDB	Air	2,425 ng/m^3
	Firemaster 680	Air	183 ng/m^3
	Tris	Air	60 ng/m^3
	Decabrom	Air	72 ng/m^3
Ethyl Corp.	EDB	Air	20,250 ng/m^3
	DBCP	Air	1,688 ng/m^3
Dow Chemical	Cl_2/Br_2	Air	64,000 ng/m^3
	EDB	Air	62,484 ng/m^3
	DBCP	Air	6,653 ng/m^3
Parkers Chapel	EDB	Air	1,260 ng/m^3
El Dorado, AK	1-Chloro-2-bromoethane	Air	4,200 ng/m^3

Table 1.3. MAXIMUM CONCENTRATIONS OF BROMINATED CHEMICALS OBSERVED IN ENVIRONMENTAL SAMPLES TAKEN IN THE VICINITY OF INDUSTRY

Vicinity of--	Chemical	Medium	Quantity
Great Lakes Chemical Corp.	Decabrom	Sediment	19,000 µg/Kg
	Bisphenol A	Sediment	22,000 µg/Kg
	Bisphenol A	Soil	150,000 µg/Kg
	Decabrom	Soil	25,000 µg/Kg
	Pentabromophenol	Soil	200 µg/Kg
	Bisphenol A	Sediment	330,000 µg/Kg
	Decabrom	Sediment	∿1,000,000 µg/Kg
Velsicol Inc.	Tetrabrom	Soil	118 µg/Kg
	Firemaster 680	Soil	253 µg/Kg
	Tris	Soil	840 µg/Kg
	Tetrabrom	Sediment	30 µg/Kg
	Firemaster 680	Sediment	466 µg/Kg
	Tris	Sediment	2,000 µg/Kg
El Dorado, AK	Bisphenol A	Human hair	>13 µg/Kg
	Decabrom	Human hair	5 µg/Kg

2.0 INTRODUCTION

Ethylene dibromide is a colorless non-flammable liquid of high density and chloroform-like odor. It is a particularly good solvent for non-polar materials such as gums, waxes and many other organic chemicals,(1) but its major use is as an additive in leaded gasoline. It is miscible with benzene, carbon tetrachloride, ether, alcohols and other non-polar solvents. Its low vapor pressure and slight water solubility suggest that it would tend to be persistent in water and soil in cases where it is released into the environment. The brominated hydrocarbons are less volatile than their chlorine analogs. Ethylene dibromide melts at about 10°C. Ethylene dibromide is commercially produced by reaction of ethylene and bromine.

The compound is generally regarded to be inert at normal temperatures and pressures with slight decomposition resulting from exposure to light.(1) At elevated temperatures, it can be hydrolyzed to ethylene glycol and bromoethanol. When heated to 340-370°C, it decomposes into vinyl bromide and hydrobromic acid. It is considered a useful synthetic intermediate since the terminal halogen atoms are reactive.

Studies indicate that ethylene dibromide is resistant to atmospheric oxidation by peroxides and ozone and a half-life of 100 days or more has been reported.(2) It is generally regarded to be less reactive in the atmosphere than the corresponding alkanes or olefins. Ethylene dibromide has a half-life of ~5-10 days in water; its hydrolysis is favored by acid conditions.(2)

Ethylene dibromide is a major industrial chemical by virtue of its use in leaded motor fuel which accounts for 85% of its demand. Domestic production of the chemical by direct combination of ethylene and bromine totaled 331 million pounds in 1973.(3) As a fuel additive (~0.025% wt/vol) ethylene dibromide serves to scavenge lead oxide residues from combustion chambers of gasoline engines.(3) Lead oxide residues result from the use of fuels containing tetra-alkyl lead compounds as anti-knock agents. The ethylene dibromide undergoes combustion with fuel. As a consequence of combustion, the bromine content of the chemical is released to the atmosphere as lead bromide through the engine exhaust. As the use of leaded fuel is abandoned, the use of ethylene dibromide in this capacity will probably also be reduced.

Another important use of ethylene dibromide has been as a fumigant for disinfecting fruits, vegetables, food grains and in warehouses.(4) It is also commonly used in conjunction with methyl bromide as a nematicide in tobacco fields where it is injected into the shank of tobacco plant stalks.(5) It also has commonly been used in citrus groves in Florida. Ethylene dibromide may be used by itself or even frequently in combination with fumigants such as carbon disulfide, ethylene dichloride and carbon tetrachloride.(6,7)

Ethylene dibromide is also a useful synthetic intermediate for the synthesis of dyes, pharmaceuticals and other organics, but these applications account for $\sim$5% of its current demand.

Similarly to ethylene dibromide, fumazone and methyl bromide are commonly used to control soil nematodes. Fumazone is a mixed halogenated hydrocarbon, i.e., dibromochloropropane.

Another extremely important area of usage of brominated organics is as fire retardants. Examples of these which are important to this program are TRIS, Decabrom and Firemaster 680. In contrast to ethylene dibromide, methyl bromide or fumazone, these are high molecular weight materials with extremely low vapor pressures and high thermal, biological and chemical stability. For these reasons these chemicals, if present, exhibit a long-term persistence in the environment and would be associated with the condensed phase matrices. Also, gradual accumulation might be anticipated with continued emissions.

The broad overview of this program has been to examine the potential prevalence of chemicals emanating from the bromine industry in the El Dorado and Magnolia, AK areas. The program was concerned with the acquisition of information about the types of chemicals associated with this industry which were in the environment for subsequent studies on their environmental impact. Although the focus has been on the monitoring of ethylene dibromide (1,2-dibromoethane) and vinyl bromide, other chemicals which might occur were also of prime interest.

The specific aims of this study were to examine environmental matrices surrounding the bromine industry in El Dorado and Magnolia, AK and to identify as much as possible all brominated chemicals resulting from industrial activities. Prior to this study a limited analysis had been conducted in this area for ethylene dibromide. However, other chemicals were not sought. For this reason, whether other brominated chemicals were being released to the environment reamined unknown. It was the objective of this study to acquire a maximum amount of information concerning the potential pollution related to the bromine industry. As part of the broad-based concept, the program was divided into a survey phase under which a limited amount of monitoring was conducted for airborne materials and the chemicals present in the environment were identified. A more in-depth study of these chemicals was to follow by examining all environmental matrices. In the survey study it was the principal objective to establish the types of chemicals associated with the bromine industry which might be released to the environment, while, in the second phase, the purpose was to determine their occurrence and quantities both immediate and distant from the plant sites. Furthermore, the specific aims eventually included determining the potential prevalence and occurrence of brominated chemicals in environmental matrices which might eventually expose local populations. However, it was beyond the scope of this program to establish a direct environmental impact by the identified brominated substances on the local vegetation and human population.

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3.0 METHOD DEVELOPMENT AND VALIDATION

3.1 INORGANICS IN AMBIENT AIR

3.1.1 Chloride/Bromide and Chlorine/Bromine Sampling and Analysis in Ambient Air

The method for collection and analysis of halides and halogens in ambient air was initially specified in the Task request as the Texas Air Control Board Method(1) for chloride and chlorine. The performance of this procedure and several supplementary analytical methods was evaluated in this laboratory for utility in the proposed study.

3.1.1.1 Evaluation of the Impinger Train for the Collection of Halides and Halogens

The impinger train specified by the Texas Air Control Board Method(1) is comprised of a midget impinger containing deionized water (20 ml) followed by an impinger containing 0.005M $NaAsO_2$ in 0.1M NaOH (20 ml). The performance of this collection system had only been evaluated for chloride and chlorine and its performance with respect to bromide/bromine was unknown. Artifacts due to the presence of chlorine or other oxidants may affect the distribution of the various halide species through the impinger train. Thus it was necessary to examine these potential problems and to validate the method prior to its implementation in this program.

The following species were tested for their distribution in the impinger train: HCl, HBr, Br_2 and Cl_2. Hydrochloric acid and HBr were introduced as aqueous solutions into an empty impinger at the beginning of the train. Volatilization occurred during the course of the experiment. The halogens were introduced by permeation tubes (Metronics Assoc., Inc., Palo Alto, CA). The permeation rates were determined gravimetrically for each tube at the temperature used for the experiments. The results are shown in Table 3.1. The last experiment in the table included the spiking of the deionized water impinger with HBr before initiating the experiment. The effluent from the

Table 3.1. EVALUATION OF HALIDE IMPINGER TRAIN PERFORMANCE

Halide species	Flow rate (ℓ/min)	Vol. (ℓ)	Midget Impingers (20 ml each)				Overall recovery
			AI[a,b] (% recovery)	AII[a,b] (% recovery)	BI[c] (% recovery)	BII[c] (% recovery)	
HCl	1.9	65.6	688 ± 48	<12			108
HCl	1.9	119	3640 ± 56	<12			
HCl	1.68	267	725 ± 4	< 6			
HBr	1.65	59.4	1176 ± 120	12			89
HBr	1.63	116	2392 ± 136	12			
HBr	1.98	283	≤1788 1700	178 164[c]			
Cl_2	0.5	31.1	94 ± 5 (84)	–	32 (29)		113
Cl_2	1.62	283	44 ± 7 (14)	–	274 ± 10 (87)	<5 (<2)	101
Br_2	1.02	28.3	27 ± 7 (54)	–	18 ± 0 (40)	–	97
Br_2	0.6	28.3	33 ± 6 (43)	–	35 ± 0 (46)		89
Br_2	1.82	300	61 ± 6 (23)	–	182 ± 0 (69)	<5 (<2)	92
Br_2	1.44	302	27 ± 6 (8)	–	29 ± 7 (85)	11 ± 1 (3)	96
HBr/ Cl_2	1.78	283	24 ± 2[d,e] (6) 348 ± 11[f] (108)				

[a] Analysis by turbidity except where stated otherwise

[b] Impingers contained deionized water

[c] Chloride determined by ion exchange chromatography

[d] Determined by fluorescein fluorescence quench

[e] Bromide determined by ion exchange chromatography

[f] Impinger AI was initially doped with 400 μg HBr

chlorine permeation tube was sampled and the deionized water analyzed by ion exchange chromatography (see Section 3.1.1.2).

3.1.1.2 Analysis of Halides and Halogens

The turbidimetric method of detection of halides in the impinger solutions is one of the more sensitive methods readily available. However, it does not differentiate between chloride and bromide. When this method is used alone, the results must be reported as total halide and in terms of the halide used for calibration (usually chloride). The response is halide-dependent as can be seen from the calibration curves shown in Figure 3.1. By using chloride for calibration purposes, the results will be underestimated by not more than 20% if the sample is pure bromide.

Separation of Chloride and Bromide.--In order to determine the specific halides present in a sample the development of an ion exchange chromatographic separation similar to that described by DeGeiso *et al*.(2) was undertaken. Following this chromatography, halide detection was made turbidimetrically.

The chromatography described by DeGeiso(2) was miniaturized and the performance evaluated as a function of column length and resin type for five 1 cm diameter columns as indicated in Table 3.2.

Table 3.2. COLUMNS EVALUATED FOR RESOLUTION OF CHLORIDE AND BROMIDE

Column	Resin Type	Mesh Size	Column Length
1	Bio-Rad AG-1 X8	100-200	4.6 cm
2	Bio-Rad AG-1 X8	100-200	6.4 cm
3	Bio-Rad AG-1 X8	100-200	10.2 cm
4	Bio-Rad AG-1 X8	100-200	13.5 cm
5	Bio-Rad AG-1 X10	200-400	8.9 cm

The resins were converted from the chloride form to the nitrate form using 0.5M $NaNO_3$. After equilibration, 5 ml of a 1.0 x 10^{-2}M NaCl solution was then placed on each column and allowed to drain, and the sides of the columns washed with 2 x 1.0 ml portions of deionized water. The column

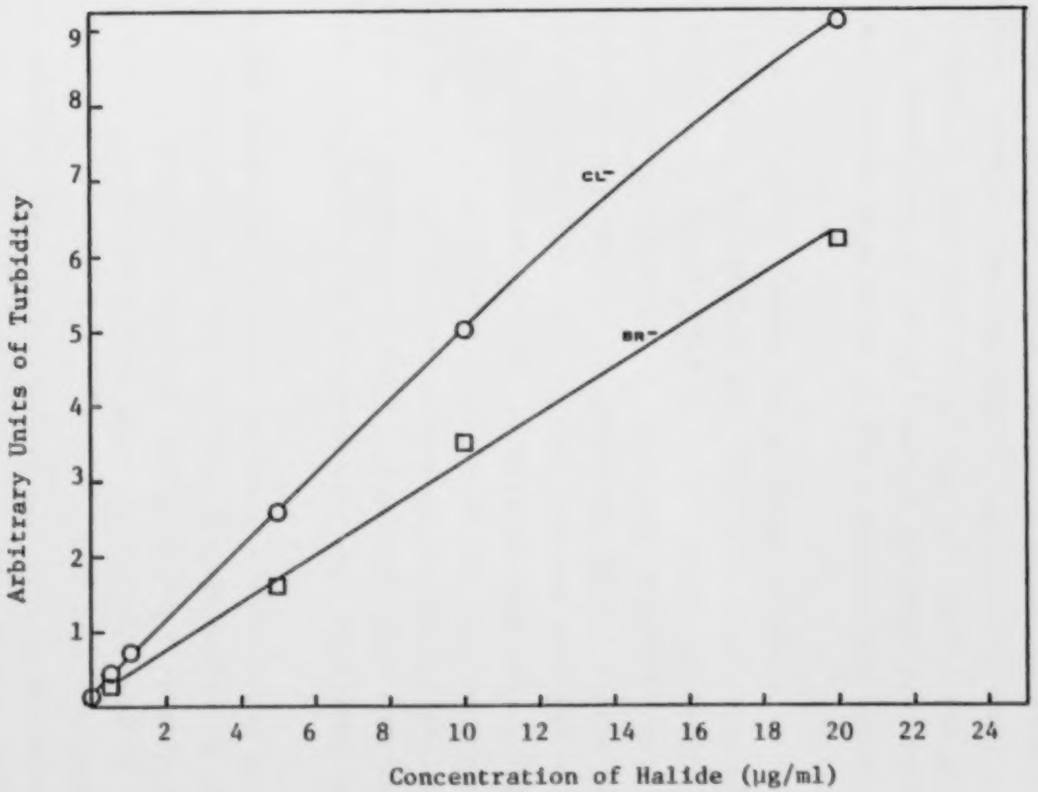

Figure 3.1. Calibration Curves for Turbidimetric Determination of Chloride and Bromide

was eluted with 0.5M $NaNO_3$ at ~1 ml/min and 2 ml fractions were collected until all the chloride was removed. Chloride concentrations were measured with a Beckmann Expandomatic 55-2 pH meter using a Beckmann chloride ion selective electrode.

The void volume of column 1 was small enough to allow breakthrough of the chloride before any of the 0.5M $NaNO_3$ eluant was passed through the column. For columns 2-5, a longer length provided a greater retention of the chloride on the column, but with only a very minor increase in peak broadness (10 ml peak width for column 2 vs. 12 ml peak width for column 4). Work proceeded with columns 2 and 3, which required less time and eluant per analysis.

The procedure above was repeated for columns 2 and 3 using 5 ml of a 1 x 10^{-2}M NaBr solution in 0.5M $NaNO_3$ and washing with 2 x 1.0 ml 0.5M $NaNO_3$. Each column was eluted with 0.5M $NaNO_3$ to the point where all the chloride had been removed as determined in the previous experiment. Then 2.0M $NaNO_3$ was passed through the column at the same 1 ml/min rate until all the bromide had been removed. Two ml fractions were collected. The bromide concentrations were measured in the same manner.

It was apparent that the use of the initial eluant, 0.5M $NaNO_3$, as the medium for application of the sample resulted in premature elution of bromide and extreme band broadening. Since adding $NaNO_3$ to the sample represents one additional step this approach was deleted from further studies.

Next to be evaluated was deionized water as the sample medium on column 3. The procedure was identical to that described above, except that the 5 ml aliquot first placed on the column was both 1 x 10^{-2}M NaCl and 1.0 x 10^{-2}M NaBr. The column sides were washed with 2 x 1.0 ml of deionized water, not 0.5M $NaNO_3$.

The bromide ion on this 10.2 cm long column began to elute just prior to changing $NaNO_3$ concentrations (see Figure 3.2). Baseline resolution was not quite attained. For this reason it was decided to lengthen the column to 15 cm.

Two impinger solutions, deionized water and 0.1M NaOH-0.005M $NaAsO_2$, were evaluated where both contained 10^{-2}M NaCl and 10^{-2}M NaBr. Two newly

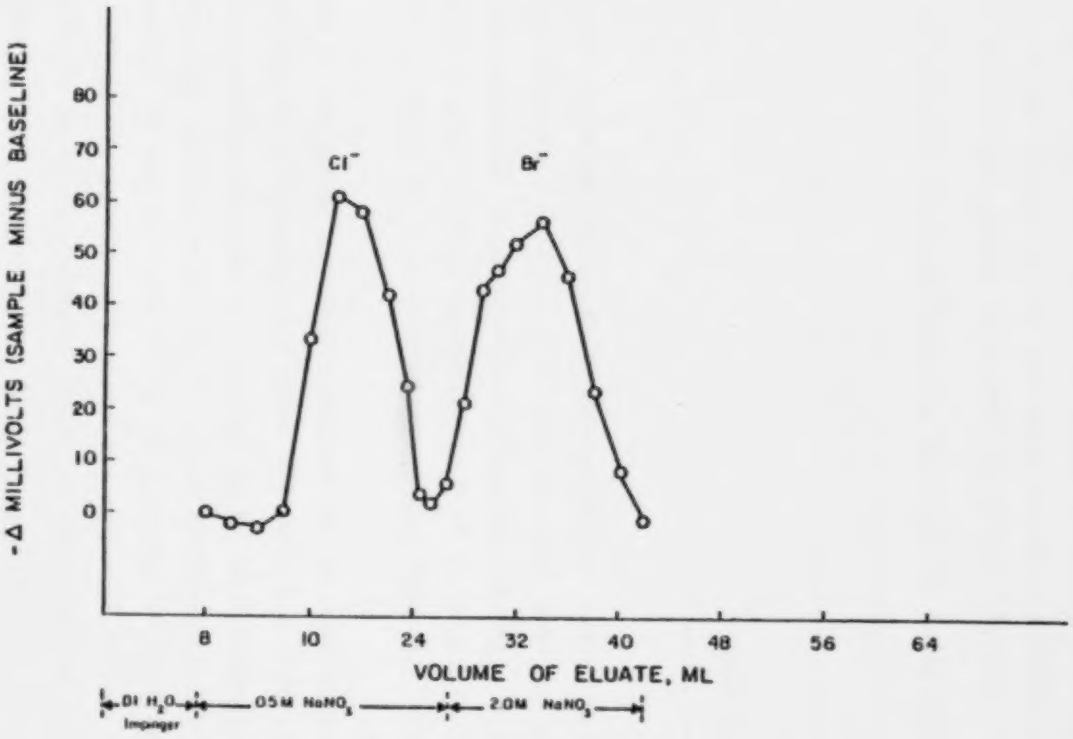

Figure 3.2. Anion exchange chromatography of Cl^- and $Br.^-$ AG-1 X8
Column: 1 cm i.d. x 10.2 cm
Concentration: 10^{-2}M

prepared AG-1 X10 columns 15 cm in length were used. Halide concentrations of each fraction were measured turbidimetrically.(1) The Texas Air Control Board Method was used with the reagent volumes reduced by 1/4 to accommodate 2 ml samples. Examples of the chromatograms obtained are shown in Figures 3.2 and 3.3 and water baseline is shown in Figure 3.4. The greatest difference in the elution pattern using the two different impinger solutions was the amount of chloride recovered from each column (see Table 3.3).

Table 3.3. RECOVERIES OF CHLORIDE AND BROMIDE FROM IMPINGER SOLUTIONS

Impinger Solution	% Recovery Cl^-	% Recovery Br^-
Deionized water	~50	~20
0.005M $NaAsO_2$-0.1M NaOH	~180	~20

A contributing factor to the amount of chloride recovered using the arsenite solution may have been the use of a prepared 0.1M NaOH solution with an unspecified chloride content (contamination). Subsequently all solutions were prepared using NaOH electrolytic pellets with a maximum chloride contaminant of .003% which corresponds to 0.12 μg/ml in the impinger solution.

A thorough assessment of the halide recoveries using ten 1-cm diameter columns of Bio-Rad AG-1 X10 (100-200 mesh) equilibrated with 0.5M $NaNO_2$ was made. Each column was 15 cm in length. Because of problems with poor recovery encountered in previous work, all of these columns were pre-equilibrated with 15 ml of solution of 10^{-2}M chloride and 10^{-2}M bromide in H_2O. The 5 ml of halide solution was drained to the top of the column, washed with 1 ml of deionized water twice, eluted with 26 ml of 0.5M $NaNO_3$, then 15 ml of 2.0M $NaNO_3$, as if an analysis were to be performed. Each column was then re-equilibrated with 0.5M $NaNO_3$ by passing 100 ml of the eluant through the column.

Five ml of the following solutions were placed on each column as indicated in Table 3.4.

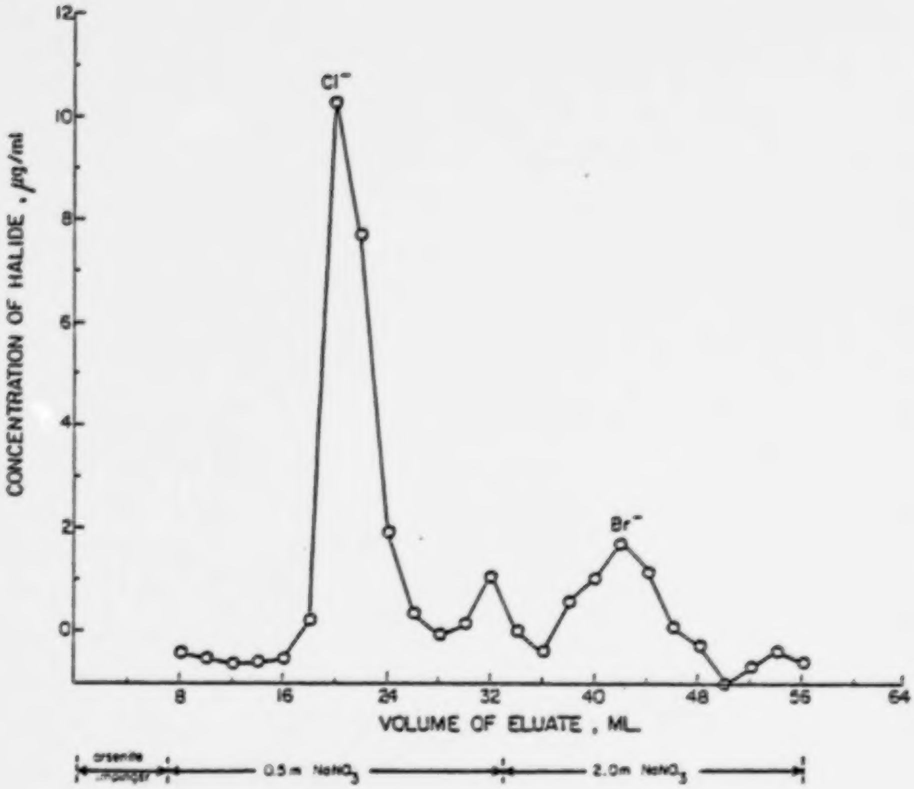

Figure 3.3. Anion exchange chromatography on AG-1 XI - Arsenite impinger solution containing chloride and bromide.
Column: 1 cm i.d. x 15 cm
Concentration: 10^{-4}M

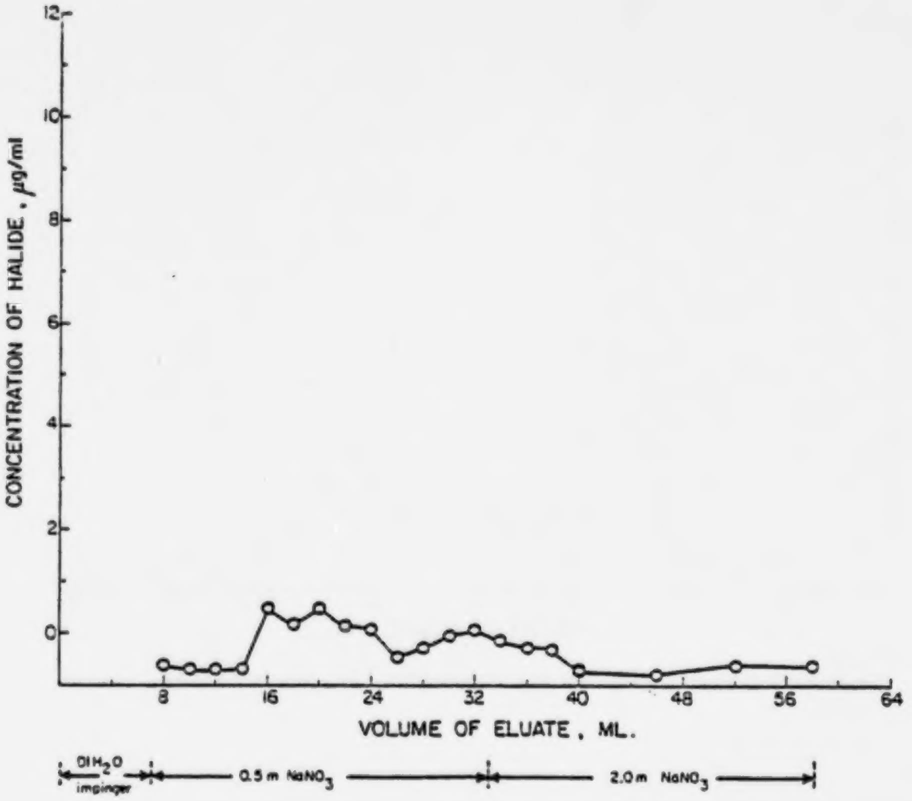

Figure 3.4. Anion exchange chromatography on AG-1 X8 - Water Blank.
Column: 1 cm i.d. x 15 cm

For each column, the procedure was to place the 5 ml of halide solution on the column and allow it to drain at 1 ml/min to the top of the column. The sides were then washed with 1 ml of deionized water twice. Twelve ml of 0.5M $NaNO_3$ were put through the column and discarded. Another 12 ml of 0.5M $NaNO_3$ were put through the column, and this was saved for analysis, as it contained the chloride fraction. Then, two more ml of this same eluant was run through and this was again discarded. The eluant was changed to 2.0M $NaNO_3$, and 15 ml was passed through the column and saved. This fraction contained the bromide. The column was then re-equilibrated with 0.5M $NaNO_3$ and was ready for further use.

Table 3.4. SOLUTIONS APPLIED TO ION EXCHANGE COLUMNS

Sample No.	Chloride (M)	Bromide (M)
1 & 8	10^{-2}	-
2 & 9	-	10^{-2}
3 & 10	10^{-4}	-
4 & 11	-	10^{-4}
5 & 12	10^{-2}	10^{-4}
6 & 13	10^{-4}	10^{-2}
7 & 14	-	-

Analysis was done as previously described(1) using the turbidimetric method.

After work was completed with the halides in deionized water, the same array of solutions was prepared using halides made up in 0.1M NaOH and 0.005M $NaAsO_2$, the halogen impinger solution. The procedure described above was followed exactly. The results are reported in Table 3.5.

The recoveries at low concentration were low and the lowest concentration tested did not approach the required level for environmental samples.

Table 3.5. RECOVERIES OF CHLORIDE AND BROMIDE FROM ION-EXCHANGE CHROMATOGRAPHY ON AG-1 X10 (100-200 MESH) 1 x 15 cm COLUMNS

Sample No.	Chloride			Bromide		
	Added (μg)[a]	Found (μg)	Recovery (%)	Added (μg)[a]	Found (μg)	Recovery (%)
1[a]	1773	940	53	-	0.05	-
2[a]	-	-0.05	-	3950	4050	102
3[a]	17.7	4.3	24	-	-0.04	-
4[a]	-	0.03	-	39.5	42.7	108
5[a]	1773	1060	60	39.5	21.3	54
6[a]	17.7	4.7	26	3950	3750	95
7[a]	-	0.45	-	-	0.10	-
8[b]	1773	1139	64	-	0.10	-
9[b]	-	1.1	-	3950	3675	93
10[b]	17.7	19.5	109	-	0.3	-
11[b]	-	12.1	-	39.5	11.2	29
12[b]	1773	950	54	39.5	18.0	45
13[b]	17.7	16.2	92	3950	3675	93
14[b]	-	0.54	-	-	0.16	-

[a] Sample was applied in 5 ml of deionized water

[b] Sample was applied in 5 ml of 0.1M NaOH/0.005M $NaAsO_2$ (impinger solution)

In an effort to improve the recoveries indicated above, new ion exchange chromatographic conditions were investigated. The rationale of the new approach was to increase specific interactions with respect to nonspecific interactions: the first system explored was DEAE Sephadex (Pharmacia, Uppsala, Sweden). The backbone of this ion exchange resin is subject to many fewer nonspecific interactions than the polystyrene-divinylbenzene backbone of the Dowex resins. The benefit of this type of backbone was not realized due to two problems: (1) the DEAE (diethylaminoethyl) functional group is weakly basic and as such does not show sufficient discrimination between chloride and bromide, and (2) the resin undergoes extreme volume changes (factors of 2 to 3) with relatively small changes in ionic strength. Another approach to increasing specific to nonspecific adsorption was to continue the use of the polystyrene-divinylbenzene type (AG-1 X10, 100/200 mesh), but to decrease the amount and use less severe conditions for developing the chromatogram. The column diameter was reduced from 1.0 cm to 0.4 cm and the length from 15 cm to 7 cm. The resin in prepared columns was converted to the nitrate form and equilibrated with deionized water. The sample was applied in 4 ml of deionized water and washed on with 0.5 ml water. The elution was begun with 0.1M $NaNO_3$ and changed to 0.5M $NaNO_3$ after the chloride had eluted (see Figure 3.5). Using the profile in Figure 3.5 a standard elution scheme was adopted: 4 ml 0.1M $NaNO_3$ for chloride and 2 ml 0.5M $NaNO_3$ for bromide. An evaluation of recoveries over a range of concentrations was instituted. The results are shown in Table 3.6. All of these samples were applied in deionized water. Certain difficulties are encountered in 0.1M NaOH/0.005M $NaAsO_2$ impinger solution. The presence of such a high anion concentration even through it is the weakly adsorbing hydroxide ion diminishes the binding of the halides during sample application and causes premature elution of the chloride and bromide peaks.

Bromide by Fluorescein Fluorescence Quench.--The method of Axelrod, Bonelli and Lodge(3) was evaluated for the analysis of impinger solutions containing bromide. The method employs hydrogen peroxide for the oxidation of bromide in an acidic medium (glacial acetic acid) to give elemental bromine. The bromine substitutes on the phenolic rings of the fluorescent

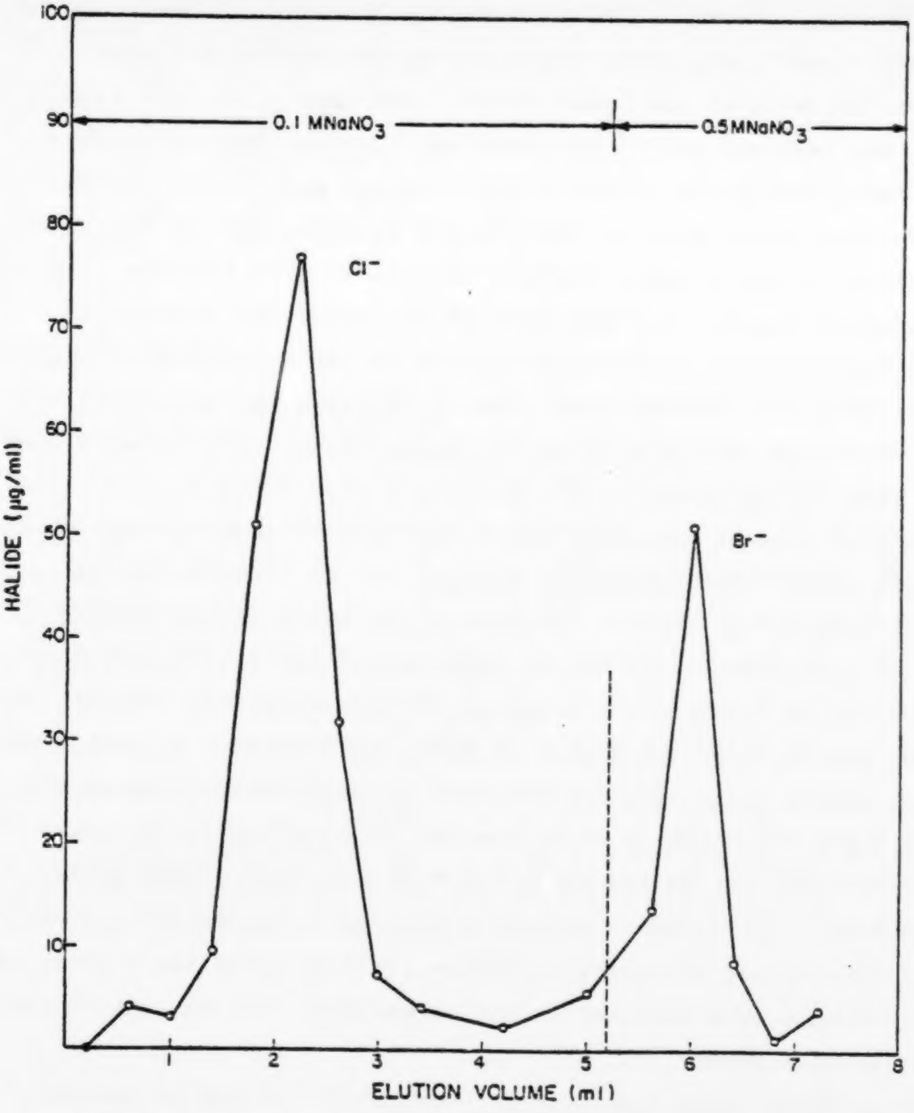

Figure 3.5. Anion exchange chromatography of chloride and bromide ions on AG-1 X10 (100/200 mesh) 4 x 70 mm column.

Table 3.6. RECOVERIES OF CHLORIDE AND BROMIDE FROM ION-EXCHANGE CHROMATOGRAPHY ON AG-1 X10 (100-200 MESH) 4 x 70 mm COLUMNS

Sample No.	Chloride			Bromide		
	added (μg)[a]	found (μg)	Recovery (%)	added (μg)[a]	found (μg)	Recovery (%)
1	500	570 ± 60	114 ± 12	0	17.8 ± 3	-
2	400	336[b]	84[b]	0	-	-
3	400	397	99.2	0	30.1	-
4	0	1.2	-	400	401 ± 2	100 ± 0.5
5	0	16.8	-	400	-	-
6	40	-	-	40	40.8 ± 1.2	102 ± 2
7	40	34.4[b]	86[b]	0	-	-
8	40	33.6	84	40	31.0	77.6
9	4	-	-	4	4.0 ± 0.2	100 ± 5
10	4	1.6[b]	40[b]	0	-	-
11	4	4.0	100	4	6.2	155
12	0	1.1 ± 0.1	-	0	1.5 ± 0.2	-
13	0	<0.8[b]	-	0	-	-
14	0	<0.8	-	0	-	-

[a] Sample was applied in 4.0 ml deionized water

[b] Collected fractions stored 48 hrs before analysis

dye, fluorescein, to yield a nonfluorescent eosin-type product. The decrease in fluorescence is measured. This procedure works well on standards in deionized water. The above authors(3) have evaluated potential interferences and found 5% or less interference due to 100 fold excess of SO_3^{2-}, SO_4^{2-}, PO_4^{3-}, NO_3^-, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, Fe^{3+}, Cu^{2+}, Pb^{2+}, HCOOH, CH_3COCH_3, HCOOH and CH_3CH_2OH. Chloride does not interfere at 10^5 molar excess over bromide. Greater than 5% error was found when I^-, NO_2^-, Fe^{2+} were present in 100 fold excess on a molar basis. Brominated organics may interfere.

Suitable conditions for the analysis of bromide in the 0.1M NaOH/ 0.005M $NaAsO_2$ impinger solution were not found. Neutralization with nitric acid and addition of 30% hydrogen peroxide before the addition of the fluorescein reagent gave no response to bromide. Some response (~70%) was observed when the bromide in impinger solution was added to the peroxide and followed immediately by the fluorescein reagent. This response is not quantitative and results would not be reliable. A cation exchange resin AG-50W-X8 was used in an attempt to neutralize the sample, but bromide recoveries from this resin were low at the 1 ppm level tested.

The final analytical protocol which was adopted for this study is given in Appendix A.

3.1.2 Determination of Inorganic Fluoride in Ambient Air

The sampling and analytical method for inorganic fluoride was specified in the research request as that adopted by the Texas State Department of Health, Air Pollution Control Board.(1)

The fluoride ion selective electrode (Orion Model 96-09 combination fluoride electrode) was evaluated over the range 1.27 to 19 ppm and found to give a linear response. Initially the samples were evaluated directly without distillation. If significant fluoride concentrations were found, then verification would have been made using the steam distillation procedure.

The final analytical protocol for collection and analysis of fluoride in ambient air which was adopted for this study is given in Appendix A.

3.1.3 Acid Mist Analysis in Ambient Air

The "acid mist" procedure(4) was verified by confirming the sensitivity of the titration to <1 μg as H_2SO_4. The residual acid on the extracted cellulose discs was <1 μg/disc as H_2SO_4.

The analytical protocol for collection and analysis of acid mist which was adopted for this research program is given in Appendix A.

3.2 Brominated Organics in Environmental Media

3.2.1 Air

3.2.1.1 Volatile Organics

Determination of Breakthrough Volumes.--The techniques for determining breakthrough volumes on solid sorbents have previously been described.(5,6) The breakthrough volumes for several halogenated compounds which had been subsequently identified in ambient air samples taken from El Dorado and Magnolia, AK were determined. It is necessary to determine the breakthrough volumes if one wishes to subsequently quantify the components identified in ambient air.

The breakthrough volumes for several brominated compounds on Tenax GC were determined at several temperatures ranging from 10-38°C (50-100°F). These results are shown in Table 3.7. Since the ambient air temperature was carefully determined during the field sampling, then the breakthrough volumes could be used for the quantification of the compounds in the samples. The breakthrough volumes were estimated at several different temperatures in the event that ambient air temperature fluctuations were experienced during sampling.

It is evident from these data (Table 3.7) that the breakthrough volumes for methyl chloride, methyl bromide, vinyl chloride and vinyl bromide are too low for utilizing this sorbent for their collection and quantification.(5) If methyl chloride, methyl bromide or vinyl bromide are detected on Tenax GC cartridges, the concentrations would be at rather elevated levels. These halogenated hydrocarbons are more suitably quantified either directly by gas chromatography with electron capture detection, or by their entrapment on carbon cartridges and subsequently detection by mass fragmentography (Ref. 5, Section E, Appendix A).

Table 3.7. ESTIMATED BREAKTHROUGH VOLUMES FOR SEVERAL HALOGENATED COMPOUNDS ON TENAX GC

		Ambient Temperatures					
Compound	BP (°C)	50°F (10°C)	60°F (15°C)	70°F (21°C)	80°F (27°C)	90°F (32°C)	100°F (38°C)
Allyl bromide*	70	37	27	20	15	11	8
Bromobenzene	155	2,144	1,521	1,079	764	542	384
Bromodichloromethane*	89-90	138	102	75	54	40	29
Bromoform	149	507	386	294	224	171	130
1-Bromopropane*	70	128	94	70	51	38	28
1-Chloro-2-bromoethane*	107	920	676	500	367	270	198
1-Chloro-3-bromopropane*	141	1,122	856	656	500	382	291
1-Chloro-2,3-dibromopropane*	-	1,460	1,114	850	649	496	378
1,1-Dibromo-2-chloropropane*	-	1,593	1,216	928	-	510	413
Dibromochloromethane*	135	263	200	153	117	89	68
1,2-Dibromoethane	131	348	255	188	138	101	74
1,2-Dibromopropane*	141	1,142	871	665	508	387	296
Methyl chloride	-24	0.8	0.6	0.5	0.4	0.3	0.25
Methyl bromide	3.59	3	2	2	1	1	0.9
Vinyl chloride	13	2	1.5	1.25	1.0	0.8	0.6
Vinyl bromide	16	8	6	4	3	2	1.8

(continued)

Table 3.7 (cont'd)

Compound	BP (°C)	Ambient Temperatures					
		50°F (10°C)	60°F (15°C)	70°F (21°C)	80°F (27°C)	90°F (32°C)	100°F (38°C)
Epichlorohydrin (1-chloro-2,3-epoxypropane)	116	200	144	104	74	54	39
Epibromohydrin (1-bromo-2,3-epoxypropane)	134-6	678	479	337	237	168	118
Trimethylene chlorobromide	142-5	1,130	927	656	465	329	233
Bromine	58.7	0.032	0.028	0.024	0.020	0.016	0.012
Chlorine	-	0.030	0.025	0.020	0.015	0.012	0.010
Iodine	184.3	0.032	0.028	0.024	0.020	0.016	0.012
Water	100	0.060	0.050	0.040	0.030	0.010	0.002

*Values estimated on mathematical extrapolation from slop of linear regression in a homologous series and boiling point of compound.

Also, the breakthrough volumes for bromine, chlorine, iodine and water are given. These inorganic gases have extremely low breakthrough volumes. This is an important feature, for if they accumulate on the sorbent, then potential in situ reactions could occur between the inorganic gases, olefinic and aromatic compounds.

Determination of Relative Molar Response Factors for Quantification.--The relative molar response (RMR) values were determined for several halogenated compounds using unique ions for each compound. The methods employed for determining the RMR values have previously been described.(5) These results are given in Table 3.8. In many cases, the RMR value for a second ion was determined in the event it would be necessary to establish the identity of the halogenated hydrocarbon by the theoretical ion cluster intensity ratio. The RMR for the second ion was calculated using authentic compounds. Thus each compound can be quantitated in the event that the first ion is not sufficiently specific for that substance.

These data (Table 3.8) also indicate that as the degree of halogenation increases, so does the RMR value, and thus a decrease in sensitivity for the compound is experienced by the mass spectrometer.

The limits of detection (LOD) for several halogenated hydrocarbons utilizing the technique of glass capillary gc/ms/comp are given in Table 3.9. The LOD's are estimated values using an average sampling volume of 150 ℓ at an ambient temperature of 27°C. The limit of detection is based upon either the breakthrough volume or volume of air sampled, whichever is less, and the measured RMR value. As shown in Table 3.9, the limits of detection for the halogenated hydrocarbons of interest range, from 0.2-2.0 ng/m^3 (sub-ppt). Table 3.9 thus provided a guideline as to the anticipated sensitivity of the overall analytical technique and was the basis for establishing the non-detectable levels. For the purpose of quantification, generally 10-20 times the amounts listed in this table were required.

The analytical protocol for collection and analysis of volatile brominated organics which was adopted for this research program is given in Appendix A.

Table 3.8. RELATIVE MOLAR RESPONSE VALUES FOR SEVERAL HALOGENATED COMPOUNDS BASED UPON SELECTED IONS

Compound	M.W.	R.R.T	1st Ion m/e (I)	1st Ion RMR	2nd Ion m/e (I)	2nd Ion RMR
Allyl bromide	120	1.167	120 (25)	3.25	122 (25)	3.25
Bromobenzene	156	2.771	156 (8)	2.18	158 ( )	-
Bromodichloromethane	162	1.389	129 (12)	1.54	85 (60)	6.16
Bromoform	250	2.361	173 (100)	2.75	252 (10)	0.30
1- or 2-Bromopropane	122	1.085	124 (20)	3.25	122 (20)	3.25
1-Chloro-2-bromoethane	142	1.657	144 (15)	1.12	63 (100)	7.39
1-Chloro-3-bromopropane	156	2.278	158 (60)	4.48	160 (120)	1.12
1-Chloro-2,3-dibromopropane	234	3.472	157 (100)	9.46	159 (25)	2.37
1,1-Dibromo-2-chloropropane	234	3.416	157 (100)	9.46	159 (25)	2.37
Dibromochloromethane	206	-	129 (100)	6.53	208 (10)	0.70
1,2-Dibromoethane	186	2.000	109 (95)	3.34	188 (2)	0.50
1,2- or 1,3-Dibromopropane	200	2.250	123 (99)	3.37	202 (65)	2.21
Methyl chloride	50	0.628	50 ( )	1.7	52 ( )	0.66
Methyl bromide	94	0.888	94 ( )	1.9	81 ( )	-
Vinyl bromide	106	0.667	108 (75)	2.2	110 (10)	0.30

Table 3.9. ESTIMATED LIMITS OF DETECTION FOR SEVERAL HALOGENATED HYDROCARBONS

Compound	Fragment ion (1st)	LOD[a] ng/m^3
Allyl bromide	120	1.6
Bromobenzene	156	0.6
Bromodichloromethane	129	2.0
Bromoform	173	0.8
1-Bromopropane	124	0.9
1-Chloro-2-bromoethane	144	0.2
1-Chloro-3-bromopropane	158	0.5
1-Chloro-2,3-dibromopropane	157	0.4
1,1-Dibromo-2-chloropropane	157	0.4
Dibromochloromethane	129	0.5
1,2-Dibromoethane	109	0.7
1,2-Dibromopropane	123	0.5

[a] Assuming an average sampling volume of 150 ℓ and 27°C which was experienced during the Phase I survey study.

Analysis of Ethylene in the Presence of Other Gases.--During the preliminary phases of this study an analytical protocol was developed for the gas chromatographic analysis of ethylene in ambient air. To effect separation of ethylene from other atmospheric hydrocarbons (e.g., ethane), the air samples were chromatographed at -78°C on an OV-101 glass SCOT capillary. Maintenance of a -78°C oven temperature was accomplished by placing small blocks of dry ice in and above the oven. This successfully lowered the oven temperature, but also resulted in the accumulation of considerable water vapor condensate in the oven and surrounding electronic components. Consequently, repeated instrument failure resulted.

Efforts to minimize condensation in the instrument centered on introduction of a dry, cold gas stream and maintenance of adequate ventilation in the oven. Initially this was accomplished by blowing a stream of nitrogen gas through a liquid nitrogen-cooled cold trap and ultimately into the gas chromatograph. This design proved troublesome as the gas line tended to freeze in the cold trap, causing the flow to be erratic. This system was modified by introducing nitrogen gas into an aspirator fixed to a metal liquid nitrogen dewar, thereby spraying a gentle, fine mist of liquid nitrogen into the oven. This technique was employed for maintaining a cryogenic oven temperature during the ethylene analyses. Difficulty was encountered in eliminating leaks from the column connections since sealed connections at 20°C tended to leak at temperatures below -60°C. Consequently, the oven was operated at -60°C with the temperature controlled by the nitrogen flow and monitored with a calibrated iron-constantan thermocouple connected with reversed polarity.

The ambient air samples, contained in stainless steel, septum-capped bottles, were introduced into a 1.7 mm i.d. x 842 mm length stainless steel gas sampling loop with a gas syringe. A minimum of 10 ml of sample was passed through the loop to insure that no contamination from previous samples would occur. The sample was injected onto a 60 m glass SCOT 1% OV-101 capillary column by changing the position of a six-way valve to direct the carrier gas (~5 ml/min) through the sampling loop. The valve and oven injection port temperatures were 170 and 0°C, respectively. Injection was sustained until the ethylene had eluted from the capillary column (approximately 2 min). Detection was achieved with a flame ionization detector operated at 150°C. Standard ethylene-nitrogen mixtures, contained in Tedlar bags, were injected every third sample for quantitation.

The final analytical protocol for collection and analysis of ethylene which was adopted for this study is given in Appendix A.

3.2.1.2 Semi-volatile Organics Associated with Particulates

Collection of Tris-(2,3-dibromopropyl)phosphate (TRIS) on Glass Fiber and Cellulose Filters -- The sampling method used for the collection of TRIS is given in Appendix A. The procedure was developed under a separate Task Order of this contract.(7) Two types of filter material, glass fiber and cellulose, were field-tested during preliminary sampling in Arkansas and the glass fiber was found to be definitely superior. Two Hi-Vol samplers in parallel were used - one fitted with cellulose filters and the other with glass fiber filters. This parallel sampling demonstrated several reasons for the choice of glass fiber.

Gas-Liquid Chromatography-Electron Capture (GLC/ECD) and Gas-Liquid Chromatography-Mass Spectrometry-Computer (GLC/MS/COMP) Analysis for TRIS -- The analytical methods used are given in Appendix A. The method was developed under a separate Task Order of this contract.(7) The approach is based upon the use of a short glass column (0.2 cm i.d. x 42 cm) packed with a nonpolar phase. The same type columns were used for both GLC/ECD and GLC/MS/COMP analyses. Three liquid phases have been used, SE-30, OV-101 and OV-17 with benzyltriphenylphosphonium chloride as a surfactant. Detection limits upon GLC/MS/COMP were very poor; hence, multiple ion detection was used almost exclusively. In this method the mass filter is stepped through discrete ion masses repetitively instead of scanning the entire mass range. The selected ions are detected for proportionately more of the total time thereby improving signal-to-noise for those ions. Confirmation of identity when required was accomplished either by monitoring several selected ions and comparing ion intensities with standards of TRIS or by direct probe MS.

Other Semi-volatile Organics Associated with Particulates -- The sampling and solvent extraction procedures developed for TRIS were used to screen for the presence of other brominated compounds. Several compounds were identified in the particulate samples by the use of direct probe mass spectrometry. Quantitation, however, requires the combination of GLC/MS/COMP analysis. In order to improve the sensitivity of the Finnigan 3300 for these high molecular weight compounds, multiple ion detection was used. Table 3.10 lists these compounds, the ions used and the instrumental limit of detection. Other factors such as collection efficiency and recovery also affect these values. First of all, the flow rate through the cellulose filter was 60% of that through the glass fiber filters and, secondly, visual inspection of the filters revealed considerable breakthrough of the particulate through the cellulose. The unexposed side of the cellulose filter was colored and a glass fiber filter which was used to support the cellulose was darkened. Mechanical strength was also a problem. The breakthrough problem was further evidenced by consistently lower values for TRIS and other brominated compounds in the cellulose filters (see 4.2.3.2). On this basis glass fiber filters were used in all subsequent sampling.

Other Analytical Methods -- Thin layer chromatography (TLC) may be used for many of the compounds which are of interest here for either a qualitative or quantitative analysis. These techniques have been used here primarily as screening methods to supplement other analytical methods. For some brominated compounds such as TRIS, the detection system reported by Weichsel(8) is useful. This method is based upon the reaction of fluorescein with elemental bromine released through peroxide oxidation. An evaluation in our laboratory of this TLC detection system has indicated that semi-quantitative results may be obtained using the technique of fluorescence quench thin-layer scanning. The basis for this detection method is the conversion of fluorescein impregnated in the thin-layer to the brominated analog, eosin. The resulting loss of fluorescence is then detected by scanning the thin-layer in the reflectance mode.(8) An example of a chromatogram obtained in this manner is shown in Figure 3.6. This detection system is highly specific for brominated compounds. However, the limit of detection is of the order of 0.5 μg/spot. Some improvement in sensitivity may be obtained by optimizing the chromatographic conditions. Basic elements of the reaction are acidic medium (glacial acetic acid), an

Table 3.10. LIMITS OF DETECTION OF BROMINATED ORGANICS IN AIR

Compound	Ions (m/e)	Limit of Detection[a,b] (ng/m^3)
TRIS[c]	417*, 419*, 337	614
Tetrabrom[d]	529*, 531*	10
Pentabromophenol	488*, 490*	25
Firemaster 680[e]	357*, 688, 690	10, 90[f]
Decabrom[g]	800*, 802, 804	20-100[h]

[a] Octachloronaphthalene was used as an external standard (m/e 404).

[b] These limits of detection are computed based upon the extract analyzed representing 2 ml/m^3 air sampled according to the procedure in Appendix A.

[c] Tris-(2,3-dibromopropyl)phosphate.

[d] 2,2-Bis(dibromo-4-hydroxyphenyl)propane.

[e] 1,2-Bis(2,4,6-tribromophenoxy)ethane.

[f] This value is based on mass 688 which was required due to interferences with mass 357.

[g] Confirmed from full scan mass spectrum.

[h] Substantial day-to-day variation of sensitivity to Decabrom.

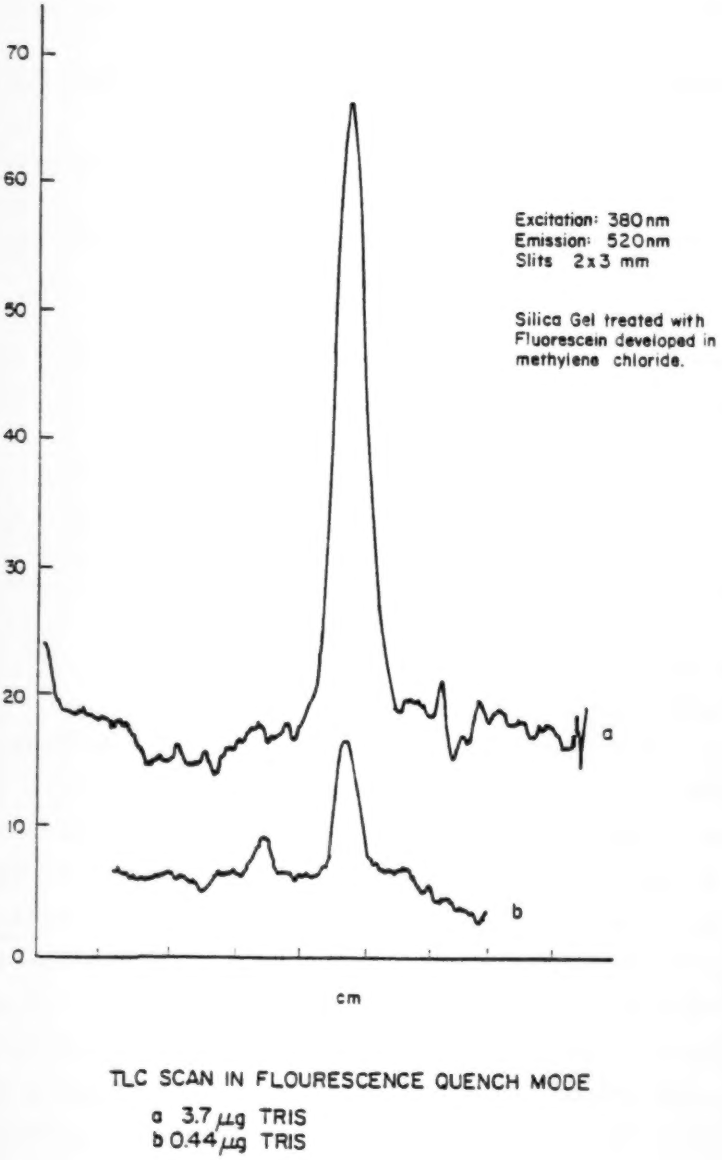

Figure 3.6. Thin layer chromatogram of tris(2,3-dibromopropyl)-phosphate on fluorescein impregnated silica gel; solvent: methylene chloride. Scan in fluorescence quench mode. a. 3.7 µg TRIS, b. 0.44 µg TRIS.

oxidant [either H_2O_2 or chloramine-T (N-chloro-p-toluene-sulfonamide)-sodium] and fluorescein. Thin-layer parameters for several semi-volatile brominated organics used throughout the program are given in Table 3.11.

Table 3.11. THIN-LAYER PARAMETERS FOR SEMI-VOLATILE BROMINATED ORGANICS ON SILICA GEL

Compound	Solvent	R_f
Decabrom	Hexane/Toluene (95:05)	0.7
2,4,6-Tribromophenol	Toluene	0.65
Pentabromophenol	Toluene	0.5
Tetrabrom	Toluene	0.4
4-Bromophenol	Toluene	0.2
Firemaster 680	Hexane/Toluene (60/40)	0.6

3.2.2 Water and Sediment

3.2.2.1 Volatile Brominated Organics

An adaptation and validation of the Volatile Organic Analysis (VOA) method was employed for the more volatile brominated compounds.

Recovery studies were performed to determine the efficiency of the purge procedure in removing various volatile organic species at approximately the 1 µg level from water and sediment. The final analytical protocols adopted are presented in Appendix A. Samples were spiked by the addition of 5 µl of a standard mixture containing ∿200 ng each of six halogenated compounds in methanol. The loaded cartridges were analyzed by GC/FID on a silanized OV-101 SCOT column (0.36 mm i.d. x 100 m length) using helium carrier at 2 ml/min. The sample was injected by thermal desorption with purging of the compounds loaded on the Tenax GC cartridge into a liquid nitrogen-cooled nickel-capillary trap. The condensed vapors are then introduced onto the high resolution gas chromatographic column by raising the temperature of the nickel capillary trap. The analytical conditions are summarized in Table 3.12. The results are given in Table 3.13.

Table 3.12. CONDITIONS FOR ANALYSIS OF TENAX CARTRIDGES FROM VOA PURGE -- RECOVERY STUDIES

GC Conditions -

Column: OV-101 (2.5%) SCOT column (0.36 mm i.d.)

Column Temperature: Programmed from 30° to 220°C at 4°/min

Detector: FID

Carrier gas: Helium

Flow rate: 2 ml/min

Thermal Desorption Conditions -

Desorption temperature: 270°C

Purge gas: helium

Flow rate: 30 ml/min

Purge time: 5 min

Ni capillary temperatures: -77°C during purge
150°C during injection

Table 3.13. RECOVERY STUDIES - VOA METHOD

Compound	Amount Spiked (μg)	Medium	Amount Recovered (μg) (1)	(2)	(3)	Average % Recovery	Standard Deviation
1-chloro-1-butene	0.926	dist. H_2O	0.710	0.743	Data	78.5	0.0233
1,2-dichloroethane	0.853	dist. H_2O	0.739	0.654	Not	81.6	0.0601
1-bromo-2-chloroethane	1.137	dist. H_2O	0.922	0.913	Available-	80.7	0.00636
1,2-dibromoethane	2.253	dist. H_2O	1.839	1.655	Intrumental	77.5	0.130
bromobenzene	1.663	dist. H_2O	1.435	1.927	Error	101.8	0.347
m-chlorotoluene	1.400	dist. H_2O	1.355	1.358		96.9	0.00212
1-chloro-1-butene	0.880	stream H_2O	0.651	0.628	0.554	69.4	0.0507
1,2-dichloroethane	0.810	stream H_2O	0.593	0.556	0.255	57.8	0.185
1-bromo-2-chloroethane	1.080	stream H_2O	1.041	1.022	1.099	96.6	0.0401
1,2-dibromoethane	2.140	stream H_2O	1.969	1.850	2.643	100.7	0.428
bromobenzene	1.580	stream H_2O	1.657	1.326	1.810	101.1	0.247
m-chlorotoluene	1.330	stream H_2O	1.337	0.999	1.074	85.5	0.178
1-chloro-1-butene	0.880	soil	0.266	0.238	0.392	33.9	0.0820
1,2-dichloroethane	0.810	soil	0.436	0.481	0.611	62.9	0.0909
1-bromo-2-chloroethane	1.080	soil	0.679	0.625	0.978	70.4	0.190
1,2-dibromoethane	2.140	soil	1.471	1.600	1.922	77.8	0.232
bromobenzene	1.580	soil	0.968	1.254	1.417	76.8	0.227
m-chlorotoluene	1.330	soil	0.881	0.830	1.134	71.3	0.163

3.2.2.2 Semi-Volatile Brominated Organics

Sample Preparation.--Two approaches to the recoveries of semi-volatile organics from water were evaluated: one, the extraction of trace organics with a macroreticular resin (XAD-2) and elution with an organic solvent (diethyl ether), and the other direct solvent partitioning. Using the procedure described by Junk *et al.* (9), recoveries of EDB and TRIS were determined using GC/ECD by comparison of peak areas with standard solutions chromatographed at the same time. The extraction method was as follows: methanol-extracted XAD-2 was placed in a column 6 mm i.d. to a height of 10 cm. The column was rinsed free of methanol with distilled water (3 x 20 ml). An aliquot (200 ml) of sample, spiked water or blank was filtered through the resin bed. The adsorbed organics were eluted with diethyl ether (25 ml) added in two portions, 15 ml and 10 ml, allowing each to equilibrate for 10 min. The ether extract was then dried over sodium sulfate and analyzed by GC/ECD. The recoveries are shown in Table 3.14. Extraction of the filtered water with diethyl ether recovered ∿ 40% of the added EDB indicating poor extraction efficiency by the resin.

Table 3.14. RECOVERIES OF BROMINATED COMPOUNDS FROM WATER USING XAD-2 RESIN

Compound	Concentration μg/ℓ	% Recoveries
EDB	1.45	12
	13.4	12
	134	8
TRIS	2.09	115
	19.3	44
	193	57

Three solvents have been screened for their extraction efficiency for EDB and TRIS. The results are given in Table 3.15. Of those tested the best solvent for EDB is hexane. Toluene is best for TRIS. A sequential extraction procedure was evaluated in which 20 ml of sample water (or spiked water) was partitioned first with 20 ml of hexane and then with 20

Table 3.15. EXTRACTION EFFICIENCY OF SEVERAL ORGANIC SOLVENTS FOR EDB AND TRIS[a]

			EDB		TRIS	
	Volume (ml)	No. of Extractions	Amount added (μg)	% Recovery	Amount added (μg)	% Recovery
Diethyl ether	40[b]	1	2.00	86	20.0	46
	20	2		<2.5		<7.5
Hexane	20	1	2.00	80	20.0	49
	20	2		<5		<15
Toluene	20	1	2.00	87	20.0	111
	20	2		<5		<15

[a] 200 ml of distilled water was spiked with the indicated amounts of EDB and TRIS.

[b] Diethyl ether was partially soluble and 40 ml was required to recover 20 ml of extract.

ml of toluene. The recoveries for each stage of this sequence are shown in Table 3.16 for TRIS and EDB. There is a problem, however, with merely combining the fractions when analyzing a volatile compound such as EDB. Toluene severely "tails" during GC analysis which affects the response of the EC detector to EDB. For this reason a parallel extraction scheme was selected for the analytical protocol (Appendix A). To verify the need to use a volatile solvent such as hexane for the analysis of volatile constituents, EDB losses upon evaporation of three solvents were compared (Table 3.17). In actual practice, only a five-fold concentration of the sample is required to detect EDB at the ppb level by GC/ECD when hexane was used.

Sediment samples were treated in the same manner as soils described in Section 3.2.3.2 except that the sample size was 10 g.

GLC/ECD and GLC/MS/COMP Analysis -- GLC/ECD methods for the semi-volatile brominated organics were developed for the purpose of method validation and sample screening. Two types of packed columns were used. A short 42 cm non-polar column (Section 3.2.1.2) for TRIS and a semi-polar column [170 cm x 0.2 cm i.d., Carbowax 20M on Chromosorb G AW/DMCS, (100/120 mesh)] for more volatile compounds such as EDB. A 42 cm x 0.2 cm i.d. column coated with 2% OV-101 on Supelcoport was used for all the GLC/MS/COMP analyses. The analytical procedure for the mass spectral analysis was the same as that described in Section 3.2.1.2. The limits of detection varied as indicated in Table 3.18.

3.2.3 Soil

3.2.3.1 Volatile Brominated Organics

The same general procedure was used for soil (and sediment) as for water except the sample size is 20 g in 450 ml of distilled water added to suspend the solids. The additional requirement for mechanical stirring to maintain the suspension was met by using a 500 ml round bottom flask and a magnetic stirrer (see Appendix A). Recovery studies were performed for soil in the same manner as for water. The results are shown in Table 3.13.

3.2.3.2 Semi-volatile Brominated Organics

Sample Preparation -- The recovery of a wide variety of compounds from a matrix such as soil poses a difficult problem. If the solvent is

Table 3.16. RECOVERIES FROM SEQUENTIAL SOLVENT EXTRACTION OF WATER[a]

	% Recovery					
	Distilled Water			Stream Water		
	Hexane[b]	Toluene[c]	Total	Hexane[b]	Toluene[c]	Total
TRIS[d]	72	15	87	91	24	115
EDB[e]	91	<10	91	82	<10	82

[a] 200 ml of sample extracted with 20 ml of each solvent.

[b] First extraction of the series.

[c] Second extraction.

[d] TRIS was added to give 100 ppb in water.

[e] EDB was added to give 10 ppb in water.

Table 3.17. LOSSES OF ETHYLENE DIBROMIDE DURING SOLVENT EXTRACTION[a]

Solvent	Concentration Factor	% Loss
diethyl ether[b]	122	14
hexane[b]	93	50
toluene[c]	15	33

[a] 100 ml of the test solvent containing 11.6 μg of EDB.

[b] Concentrated in Kuderna-Danish (K-D) apparatus and micro K-D on steam bath. Snyder columns were used throughout.

[c] Concentrated in flat bottom flask using Snyder column and a hot plate for heat.

Table 3.18. LIMITS OF DETECTION OF BROMINATED ORGANICS IN WATER

	Method		
Compound	GLC/ECD (μg/ℓ)	GLC/MS (μg/ℓ)	Other (μg/ℓ)
EDB	1	-[a]	-
TRIS	0.2	500-1000	20[b]
Tetrabrom	-	50	-
Pentabromophenol	-	100	-
Firemaster 680	-	50[c], 800[d]	-
Decabrom	-	10	2.5

[a] Not determined.

[b] Thin-layer chromatography.

[c] Based upon m/e 257, a non-specific ion.

[d] Based upon m/e 688, the parent ion.

not selective for the compound of interest the background may be seriously elevated and extensive clean-up procedures required. With this in mind, two soil extraction procedures were evaluated. One employed a water/acetonitrile/ ethyl ether partition and the other water/acetone/toluene. A soil sample (50 g) was wetted with 50 ml of water and extracted with 50 ml of acetonitrile/ ethyl ether (1:1) followed by two 50 ml ethyl ether extractions. Recoveries from the first solvent combination were very low (<10%) for decabromobiphenyl ether (Decabrom) and EDB, two of the three compounds selected as "marker" compounds for this evaluation. The latter solvent combination proved more satisfactory. In this procedure, 50 g of soil was extracted with 50 ml of diethyl ether; 10% of this extract was reserved for volatiles (EDB) analysis with the remainder combined with subsequent fractions. Ether extraction was followed by the addition of water (5 ml), acetone (40 ml) and toluene (80 ml) and mixing. The organic layer was removed and filtered. The acetone and toluene extraction was repeated two more times and the volume reduced before GC/ECD analysis. Table 3.19 gives the recoveries for selected compounds.

Table 3.19. RECOVERIES OF SEMI-VOLATILE HALOGENATED ORGANICS FROM SOIL BY SOLVENT EXTRACTION[a]

Compound	Concentration µg/ℓ	% Recoveries
1,2-Dibromoethane	1000	52
	100	7.9[b]
Tris-(2,3-dibromo-propyl)phosphate	1000	81
	100	77
Decabromobiphenyl ether	1000	85
	100	84

[a] Method of extraction described in the text.

[b] An evaporation step was employed which may be responsible for the loss of EDB. This step has since been found to be unnecessary for GC/ECD analysis.

GLC/ECD and GLC/MS/COMP Analysis of Soil Extracts -- The GLC/ECD methods described in Section 3.2.2.2 were applicable to screening of soil samples for TRIS. Where very high levels were present, TLC methods for

Decabrom were used. In general, however, GLC/MS/COMP was used in the MID mode for the analysis of soil sample extracts. The same conditions were used as those described in Section 3.2.1.2. Limits of detection were higher than for water by a factor of 2 to 3.

3.2.4 Other Media

3.2.4.1 Hair

Samples were extracted in a Soxhlet apparatus with toluene for 16 hrs and the volume reduced to 5-10 ml using a Snyder column. Aliquots (0.5 ml) were evaporated to dryness and weighed to determine total solids (oil). Octachloronaphthalene was added to each sample as an internal standard. These aliquots were redissolved and purified using high performance liquid chromatography on a μStyragel (500Å) column with toluene as a solvent. Prior to sample analysis the elution volumes of several marker compounds were established (Decabrom and Firemaster 680) and these elution volumes were used to select the fraction collected. Two chromatographs of 50 to 100 μl of extract (~4-8 mg of hair oil) were performed on each sample. The fractions from each sample were combined and the volume reduced for submission to GC/MS/COMP analysis. The same GLC/MS analysis conditions were used as for the soil and sediment samples.

3.2.4.2 Milk

Several attempts at direct solvent extraction were unsuccessful due to emulsion formation. However, the following procedure was successful. A well-mixed weighed sample (10 g) was mixed with clean glass wool and the proteins precipitated by the addition of 100 ml of acetone. Separation of the precipitate was sometimes facilitated by centrifugation. The acetone was decanted and filtered as were two additional 25 ml acetone fractions. The volume of the acetone was reduced to ~20 ml using a Snyder column. The precipitate was washed two times with 10 ml of toluene. The toluene fractions were combined with the acetone. Two phases formed due to the water in the acetone and the aqueous phase was removed. The organic phase was dried over sodium sulfate and the volume reduced to 5-10 ml. This procedure was followed using blank raw cows' milk and milk which was spiked in the amounts given in Table 3.20.

Table 3.20. AMOUNTS OF BROMINATED ORGANICS ADDED TO MILK

Compound	MB	Sample M1 (μg/g)	 M10 (μg/g)
2,4,6-Tribromophenol	0	1.2	12
Tetrabrom	0	1.0	10
TRIS	0	2.4	24
Decabrom	0	1.0	10

Figure 3.7 shows the elution volumes of several brominated compounds relative to sample MB (Figure 3.7-F). Figure 3.8 shows the chromatogram for M10 with both uv (300 nm) and refractive index (RI) detection. The chromatogram of the M1 extract showed some of the appropriate peaks on the UV detector but the RI detector is too insensitive to detect TRIS at this level (1.1 μg). The other brominated compounds such as Decabrom and tribromophenol, were clearly present in the expected amounts.

3.2.4.3 Placenta

The placenta samples were extracted by the same procedure as used for the milk samples with the addition of homogenization with a Virtis Blender after the addition of acetone. HPLC clean-up was attempted on the placenta extracts; however, the lipids in this case appeared to be relatively low molecular weight compared to milk (see Figure 3.9).

3.3 References

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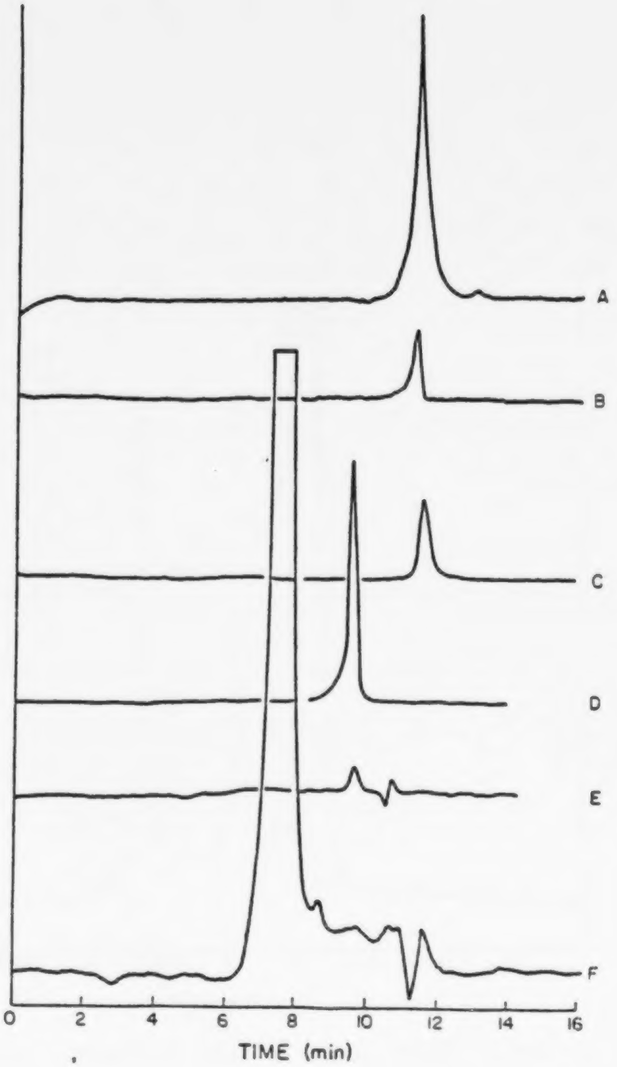
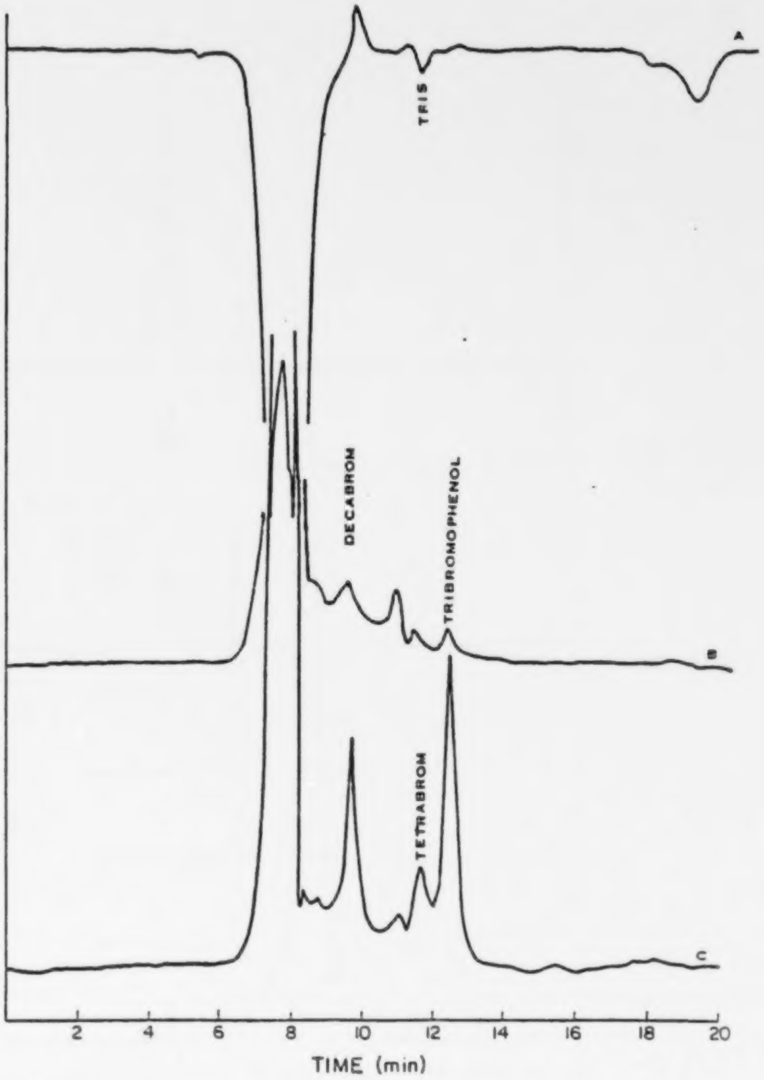


Column: μStragel (28 cm); Solvent: Toluene
Flow rate: 1 ml/min; UV: 300 mm

Figure 3.7. Retention volumes of some brominated compounds on HPLC. A - TRIS (466 μg), RI detector, x8; B - 1-chloro-2,3-dibromopropane (118 μg), RI detector, x8; C - tetrabrom (40 μg), uv detector, 0.4 AUFS; D - decabrom (40 μg), uv detector, 0.4 AUFS; E - hexabromodiphenyl (2 μg), uv detector, 0.1 AUFS; F - blank milk extract.



Column: μStyragel (28 cm); Solvent: toluene;
Flow rate: 1 ml/min; UV: 300 nm - 0.1 AUFS;
RI: 8X

Figure 3.8. High performance liquid chromatography of spiked milk extracts: A - extract M10 (200 μl injected or 4% of extract); RI detector; B - Extract M1 (100 μl injected or 4% of extract), UV detector; C - Extract M10 (200 μl injected or 4% of extract), UV detector.

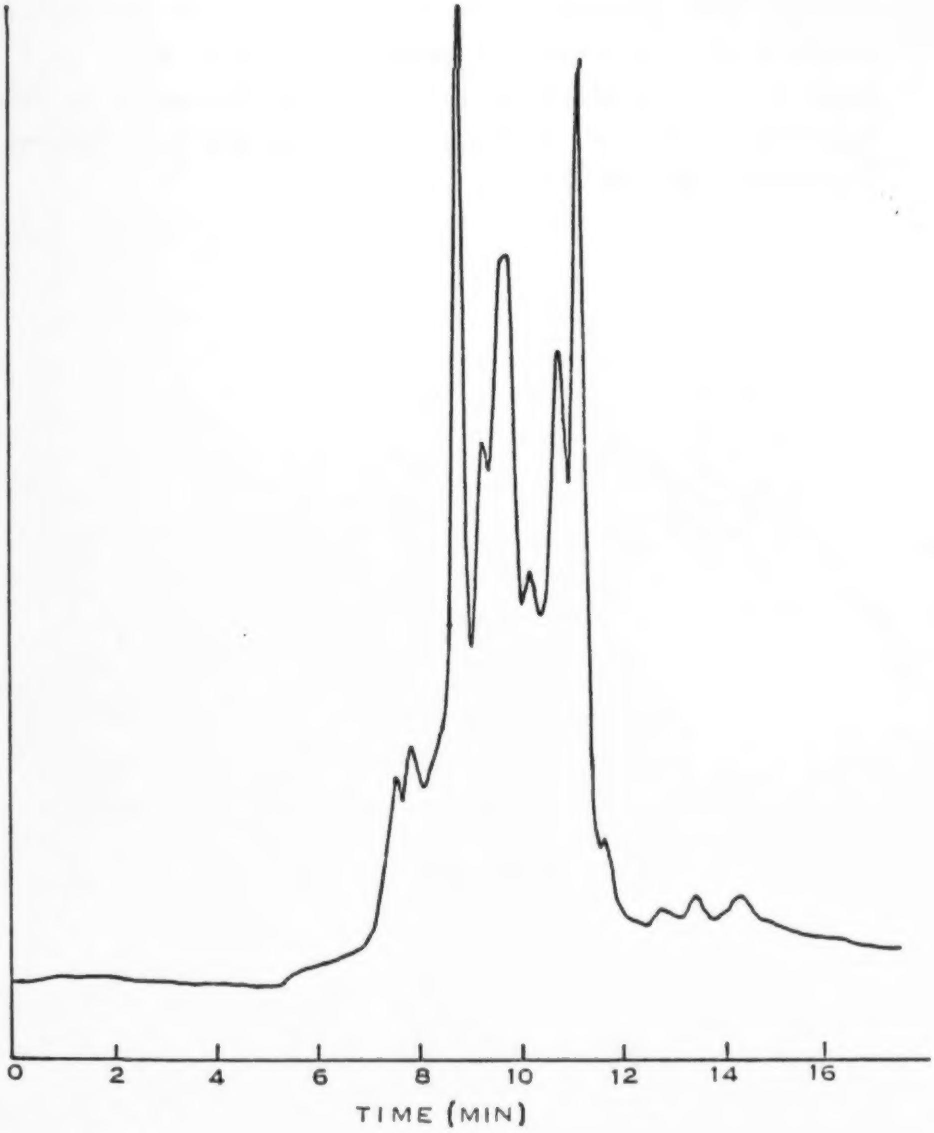


Figure 3.9. Placenta extract - hplc chromatogram of μStyragel column.

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4.0 SURVEY OF ENVIRONMENTAL MEDIA FOR CHEMICALS ASSOCIATED WITH BROMINE INDUSTRY

4.1 TECHNICAL STRATEGY

The strategy which was adopted for the Survey Phase attempted simultaneously to evaluate the analytical techniques employed for characterizing the ambient air and to acquire a maximum amount of information about the chemicals surrounding the bromine industry.

The analytical methods utilized in this study are given in Table 4.1. Scanning electron microscope (SEM) equipped with energy dispersing X-ray (EDX) capabilities (Section A, Appendix A) was used for element mapping of particles collected on glass and cellulose fiber filters. Primary application of SEM and EDX was for detecting the presence and relative amounts of Cl, Br, S, and counterions (Na, K, Ca, etc.).

Table 4.1. ANALYTICAL TECHNIQUES EMPLOYED FOR STUDYING POLLUTANTS IN AMBIENT AIR SURROUNDING BROMINE INDUSTRY IN ARKANSAS

Technique	Information Type
Scanning Electron Microscope and Energy Dispersive X-ray Analysis	Cl, Br, counterions, particle topography
Neutron Activation Analysis	Total Cl, Br
Spectrophotometric Techniques	$Cl^- + Br^-$, Cl^-, Br^-
Gas Chromatography Flame Ionization Detection	Ethylene
Gas Chromatography Electron Capture Detection	Methyl chloride, Methyl bromide
High Resolution Gas Chromatography/ Mass Spectrometry/Computer	Structural characterization and quantification of volatile organics

Neutron activation analysis (Section B, Appendix A) was employed for determining the total Cl and Br content in various collected sample matrices. Depending on the information type desired semi-quantitative and quantitative data were obtained where possible.

Turbidity measurements (Section G, H, Appendix A) were made for total halide (and halogen) and when feasible individual species were quantitated after applying ion-exchange methods. In some cases neutron activation, SEM, and EDX were used in concert with spectrophotometric methods (Sections I, J, and Appendix A).

A variety of gas chromatographic methods was employed with specific detectors for organic analysis. Flame ionization was employed for ethylene analysis (Section C, Appendix A). Methyl chloride and methyl bromide were detected by electron capture (Section D, Appendix A).

For obtaining a broad overview of the types of organics and the levels present in ambient air, high resolution gas chromatography/mass spectrometry/computer techniques were used (Section E, F, Appendix A).

4.1.1 Sampling

In order to cross-check the analytical techniques, sampling efforts were designed to acquire sufficient quantities of samples (replicates) for multi-analyses. Figure 4.1 depicts a schematic of the cartridge sampling train used for fractionating non-volatile, semi-volatile and volatile components from ambient air. A glass fiber filter preceded the Tenax GC cartridge. The filter was used for removing non-volatile or particulate material from the air. The volatiles were trapped on Tenax GC. In tandem with the Tenax GC cartridge we used an SKC carbon as a back-up material for stopping the very volatile organics (e.g., vinyl chloride, vinyl bromide, methyl chloride and methyl bromide).

Molecular chlorine, bromine and the halides, chloride and bromide, were collected in midget impingers (Figure 4.2) in a tandem arrangement (Sections G, H, Appendix A). Sufficient impinger volumes were used in the collection scheme for subsequent multi-analyses. Fluoride was collected in a separate, single midget impinger concomitantly and in parallel with the Cl/Br devices (Section I, Appendix A).

Acid mist was collected on cellulose filters and in duplicate (Section J, Appendix A).

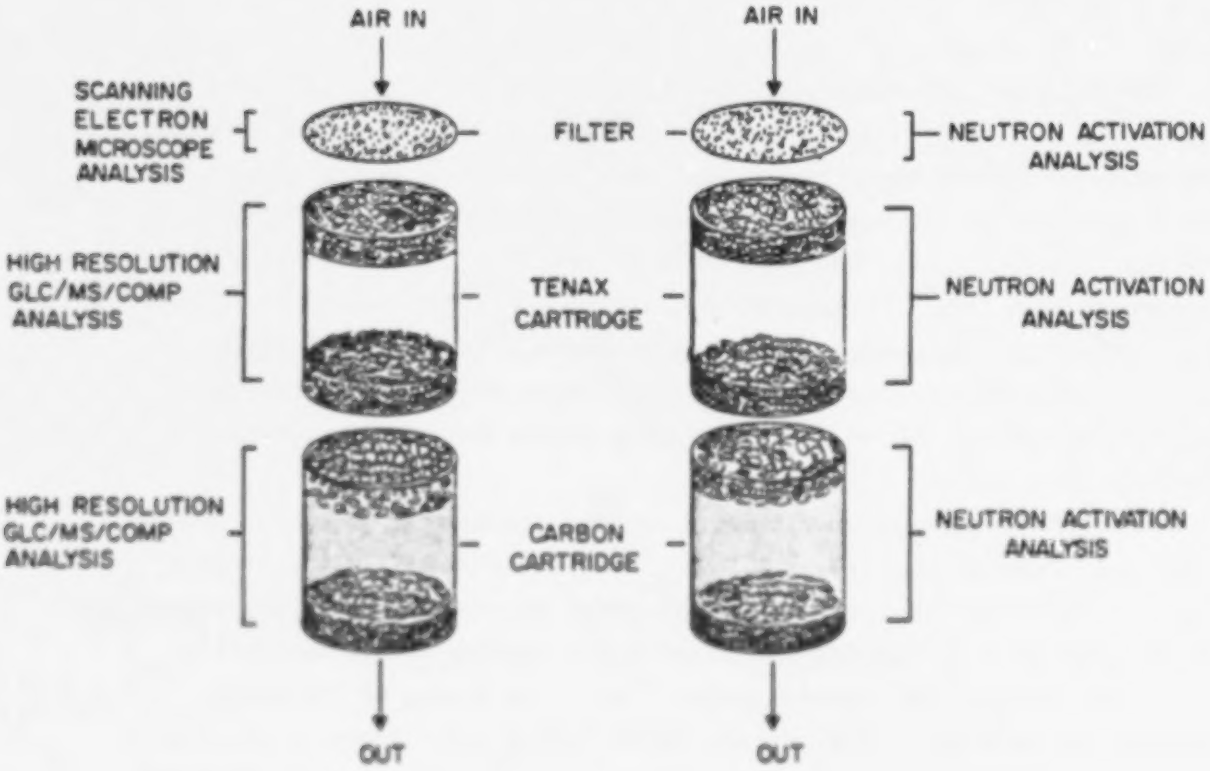

AIR IN
AIR IN
SCANNING ELECTRON MICROSCOPE ANALYSIS
FILTER
NEUTRON ACTIVATION ANALYSIS
HIGH RESOLUTION GLC/MS/COMP ANALYSIS
TENAX CARTRIDGE
NEUTRON ACTIVATION ANALYSIS
HIGH RESOLUTION GLC/MS/COMP ANALYSIS
CARBON CARTRIDGE
NEUTRON ACTIVATION ANALYSIS
OUT
OUT

Figure 4.1. Schematic of duplicate (parallel) cartridge sampling and designated sample analysis

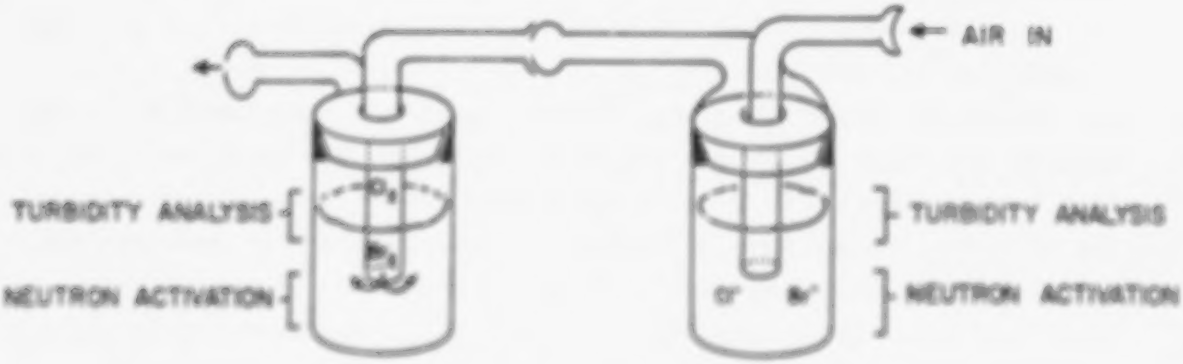

AIR IN
TURBIDITY ANALYSIS
NEUTRON ACTIVATION
TURBIDITY ANALYSIS
NEUTRON ACTIVATION
Cl⁻
Br⁻

Figure 4.2. Tandem midget impingers for collection and designated sample analysis for halogenated substances

Hi-Vol glass and cellulose fiber filters (Figure 4.3) were used for collecting particulates for SEM and EDX analysis. As part of the sampling protocols in each of these cases, "Hi" and "low" volume cartridge sampling was performed with the intent of collecting adequate quantities of material for characterization by high resolution GLC/MS/COMP. A Nutech Model 221-A sampler (Nutech Corp., Durham, NC) was utilized for "Hi" volume sampling and a DuPont personal sampler (Section F, Appendix A) for "low" volume sampling. The DuPont sampler was also evaluated for potential long-term sampling (24-36 hr) and sampling in highly remote and distant locations from the plant sites.

The DuPont samplers were located off the property of the Great Lakes Corp. and Arkansas Chemical, Inc. area. They were placed on the water tower in Parker's Chapel and on a water tower in downtown El Dorado, Arkansas. The purpose of this sampling was to determine whether it was possible to detect and quantify halogenated organic volatiles during an overnight period. We intended to demonstrate whether halogenated organic vapors were transported from the plant sites to populated areas resulting in potential exposure. The Parker's Chapel water tower is located between Great Lakes Corp. and Arkansas Chemical, Inc. on Arkansas Highway 15. It is approximately one mile from Great Lakes (line of sight) and about 1.5 miles from Arkansas Chemical, Inc.

Inorganics were collected during separate sampling periods at the same locations as for organics.

During all sampling periods, meteorological data were recorded continuously at one sampling location with a Meteorological Research, Inc. instrument (temperature, wind direction and speed). Every 30-60 min, wind speed and direction, temperature, barometric pressure and humidity were recorded using hand-held instrumentation. These parameters were estimated with a Dwyer Wind Meter (Dwyer Inst. Inc., Michigan City, IN), a pocket altimeter (Giechard, West Germany), and a sling psychrometer (Taylor Inst. Co., Rochester, NY). Direction bearings and distances were measured with a lensatic compass and a Rangematic Distance Finder (Ranging Inc., Rochester, NY), respectively.

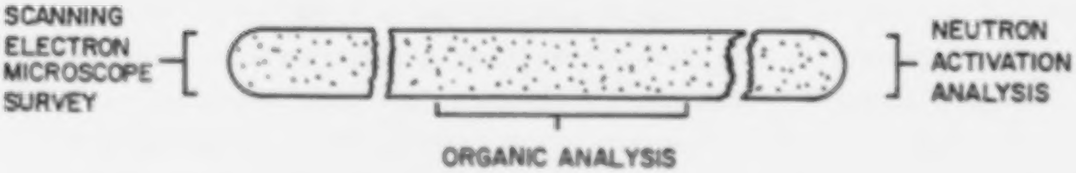

SCANNING ELECTRON MICROSCOPE SURVEY
NEUTRON ACTIVATION ANALYSIS
ORGANIC ANALYSIS

Figure 4.3. Hi-Vol filter and designated sample analysis

Other subjective observations were also made.

4.1.2 Analytical Cross-Checking

In order to evaluate the analytical methodology and to obtain a broad spectrum of information concerning potential pollutants, several instrumental techniques were used in a cross-check fashion. The glass fiber filters (Figure 4.3) from the cartridge sampling train were examined by SEM, EDX (when feasible) and NA techniques. Using this approach it would be possible to determine the relative amounts of Cl, Br, and S occurring in the non-volatile fraction (particulate) and to a certain degree whether these elements are predominantly organic or inorganic by counterion studies using SEM-EDX. The use of SEM-EDX and NA also serves as a rapid preliminary screening technique to determine whether analysis for organics, inorganics or both is justified by other more definitive (but time-consuming) methods.

The volatile organic compounds trapped on the Tenax cartridge were designated for analysis by high resolution GC/MS/COMP techniques and by neutron activation (Figure 4.1). High resolution GC/MS/COMP analysis of the Tenax cartridge allowed the identification and quantification of organic volatiles which were emitted by the bromine extraction or synthetic organic units at the plant facility. In some cases duplicate analysis of the Tenax cartridges by high resolution GC/MS/ COMP was conducted in order to determine the reproducibility of analysis. In other cases, a second cartridge was not subjectd to high resolution GC/MS/COMP analysis, but instead submitted for neutron activation. In this manner, it was possible to determine whether chlorinated and brominated compounds escaped detection by the high resolution C/MS/COMP analysis since it was possible by the more general technique of neutron activation to obtain total equivalents of Cl and Br. Carbon cartidges (Figure 4.1) were analyzed similarly to the Tenax cartridges, by igh resolution GC/MS/COMP and by neutron activation analysis.

Although high resolution GLC/MS/COMP was used for unequivocal identification of vinyl chloride, vinyl bromide, methyl chloride and methyl bromide from Tenax C cartridges, these halogenated compounds were also quantified by independent methods, *i.e.*, GC with electron capture (Section D, Appendix A) and massfragmentography (Section E, Appendix A).

In addition to the sampling of low volumes (~75-150ℓ) of air with the cartridge train, Hi-Vol sampling was employed (Figure 4.3). Glass and cellulose filters were subjected to SEM-EDX and NA analysis.

The first impinger solution contained primarily halides (Figure 4.2) and was examined by NA and turbidity methods. In some cases, ion-exchange separation of Cl^- and Br^- was performed to determine individual halide concentrations in air. The second impinger trapped molecular chlorine and bromine; it was treated in the identical manner to the first.

4.1.3 Prioritization of Sample Analyses

Many samples were taken for organic and inorganic analyses. Since the major objectives of this study were to obtain a broad overview of the major pollutants occurring from the bromine industry and to evaluate analytical techniques for collection and analysis, samples were prioritized and "best samples" were examined. These were selected on the basis of the best sampling conditions as reflected by the meteorological parameters during the sampling period. Also, consideration was given to significant potential emissions during the most active periods of the plant facility operations. Lower priority was given to those cases where the plant operations were believed to be unfavorable for collection of adequate amounts of chemicals for study. Furthermore, when meteorological conditions were unstable or when emissions from the plant sites were not continuously carried to the sampling locations, the samples were given a low analysis priority.

The prioritization scheme for the Survey Phase was necessary to obtain a maximum amount of information with the expenditure of only a moderate level of effort.

4.2 RESULTS AND DISCUSSION

4.2.1 Arkansas Chemical Incorporated

4.2.1.1 Sampling

The sampling protocol and sample descriptions for Arkansas Chemical Inc. are given in Table 4.2. The corresponding Figures 4.4 and 4.5 designate the sampling locations for September 20 and 21, 1976. Soil and water samples were also collected on April 4, 1977. These protocols are given in Table 4.3 and Figure 4.6.

Table 4.2. SAMPLING PROTOCOL FOR ARKANSAS CHEMICAL INCORP., HIGHWAY 15, EL DORADO, ARKANSAS

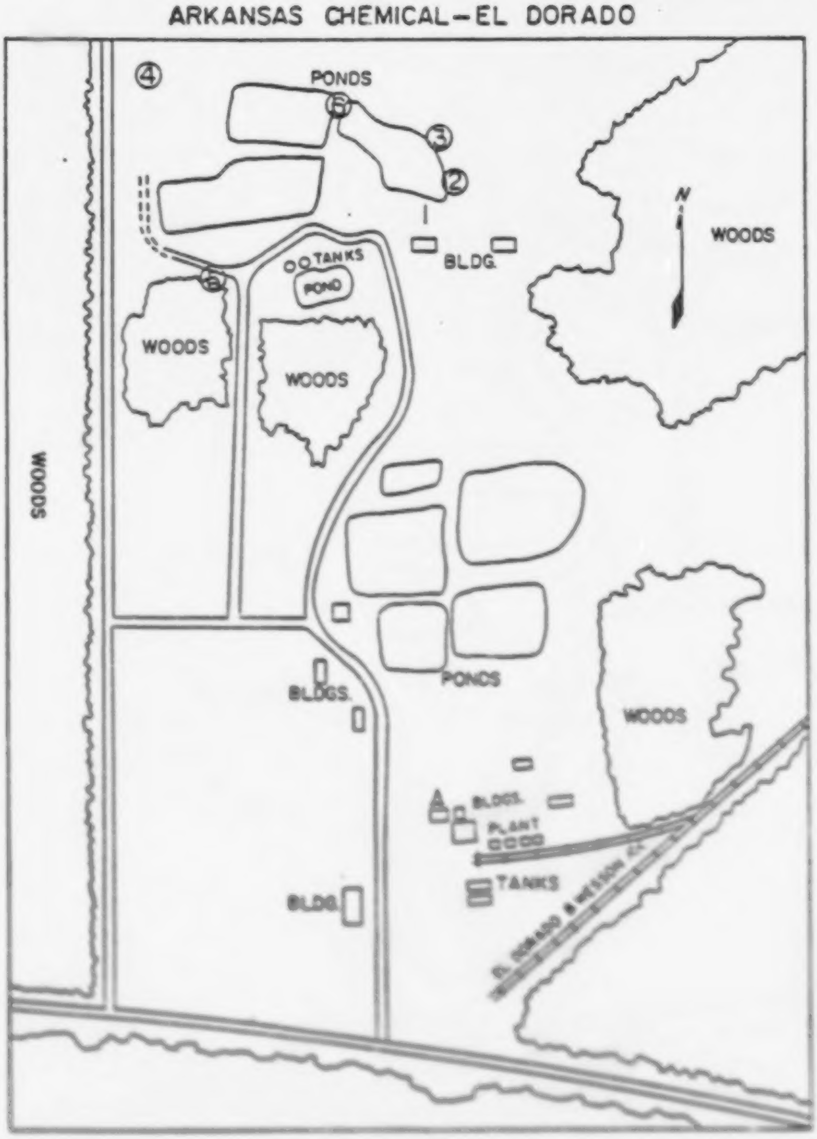
Period	Cycle	Location	Sampling Time	Sampling Volume (ℓ)	Type of Sample	Meteorological Conditions			
						T (°C)	% RH	Wind Dir./ Speed (kmph)	Other
[illegible]	C1	L1	1130-1523	103	HHC^a	25-26	95	270°/6	Full Cloud Cover, rain
		L2	1130-1525	102	HHC^a	25-26	95	270°/6	Full Cloud Cover, rain
		L3	1130-1530	137	HHC^a	25-26	95	270°/6	Full Cloud Cover, rain
		L4	1325-1526	148	HHC^a	25	95	270°/6	Full Cloud Cover, rain
	C2	L1	1545-1616	44	F, CBN, CBD				
		L2	1545-1616	54	F, CBN, CBD				
		L3	1545-1615	43	F, CBN, CBD				
		L4	1545-1615	81	F, CBN, CBD				
	C3	L1	1637-1800	272	AM				
		L2	1637-1757	154	AM				
		L3	1640-1750	137	AM				
		L4	1636-1750	90	AM				
		L1	1720	1	TED				
		L2	1742	1	TED				
		L5	1740	1	TED				
		L1	1723	0.28	VAC				
		L5	1727	0.28	VAC				
		L4	1727-1742	0.28	VAC				
[illegible]	C1	L1	1005-1035	184	HHC^a	27	44		
		L2	1000-1026	235	HHC^a				Odor of H_2S, Br_2
		L3	1000-1035	243	HHC^a				Clear

[a] Bendix Model 220 sampler 3-6 ft elevation.

Locations shown in Figures 4 and 5.

Key to Sample Type:

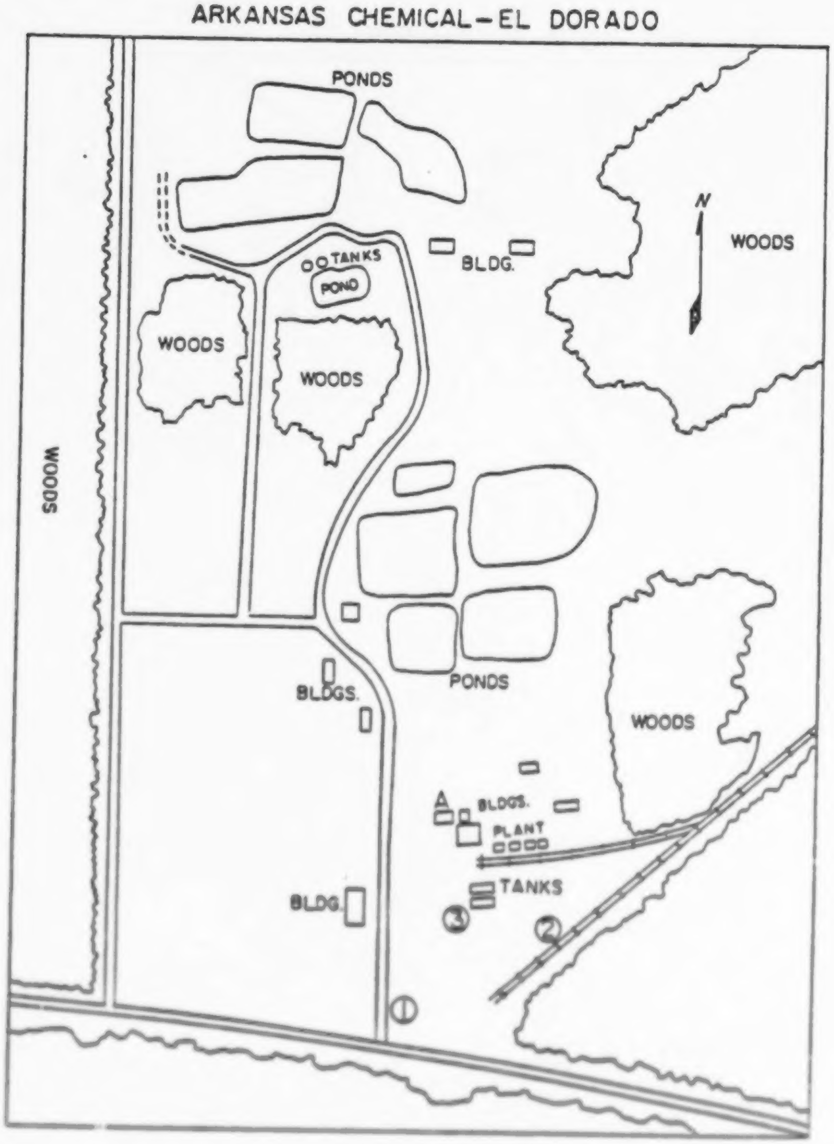
HHC - Halogenated Hydrocarbon
F - Fluorine and Fluoride
CBN - Bromine and Chlorine
CBD - Bromide and Chloride
AM - Acid Mist
TED - Tedlar Bag
VAC - Aluminum Vacuum Can


ARKANSAS CHEMICAL—EL DORADO
④
PONDS
⑤
③
②
⑥
TANKS
POND
BLDG.
N
WOODS
WOODS
WOODS
WOODS
PONDS
BLDGS.
WOODS
A
BLDGS.
PLANT
TANKS
BLDG.
EL DORADO & WESSON RR.

APPROX. SCALE 1 cm = 110 m

Figure 4.4. Schematic map of Arkansas Chemical Incorp., El Dorado - sampling locations for F1 - 9/20/76.

A - Br_2 facility


ARKANSAS CHEMICAL-EL DORADO
PONDS
TANKS
POND
BLDG.
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WOODS
WOODS
WOODS
WOODS
PONDS
BLDGS.
WOODS
A
BLDGS.
PLANT
TANKS
BLDG.
③
②
①

APPROX. SCALE 1 cm = 110 m

Figure 4.5. Schematic map of Arkansas Chemical Incorp., El Dorado - sampling locations for P2 - 9/21/76.

A = Br_2 facility.

Table 4.3. SAMPLING PROTOCOL FOR ARKANSAS CHEMICAL INCORP., EL DORADO

Period	Cycle	Location	Sample Size	Type of Sample
1	C1	L1	2 cores	SHHC-V
4/7/77			2 cores	SHHC-SV
		L2	2 cores	SHHC-V
			2 cores	SHHC-SV
		L3	2 cores	SHHC-V
			2 cores	SHHC-SV
			1 ℓ	WHHC-V/SV[a,b]

[a] Stream 30 cm wide, 10 cm deep in drainage ditch.

[b] Water was collected from standing puddles.

Key to sample type:
SHHC - soil for halogenated hydrocarbons
WHHC - water for halogenated hydrocarbons
VHHC - vegetation for halogenated hydrocarbons
SEHHC - sediment for halogenated hydrocarbons
SCHHC - scum on water for halogenated hydrocarbons
MHHC - milk for halogenated hydrocarbons
V - for volatile organic analysis
SV - for semi-volatile organic analysis

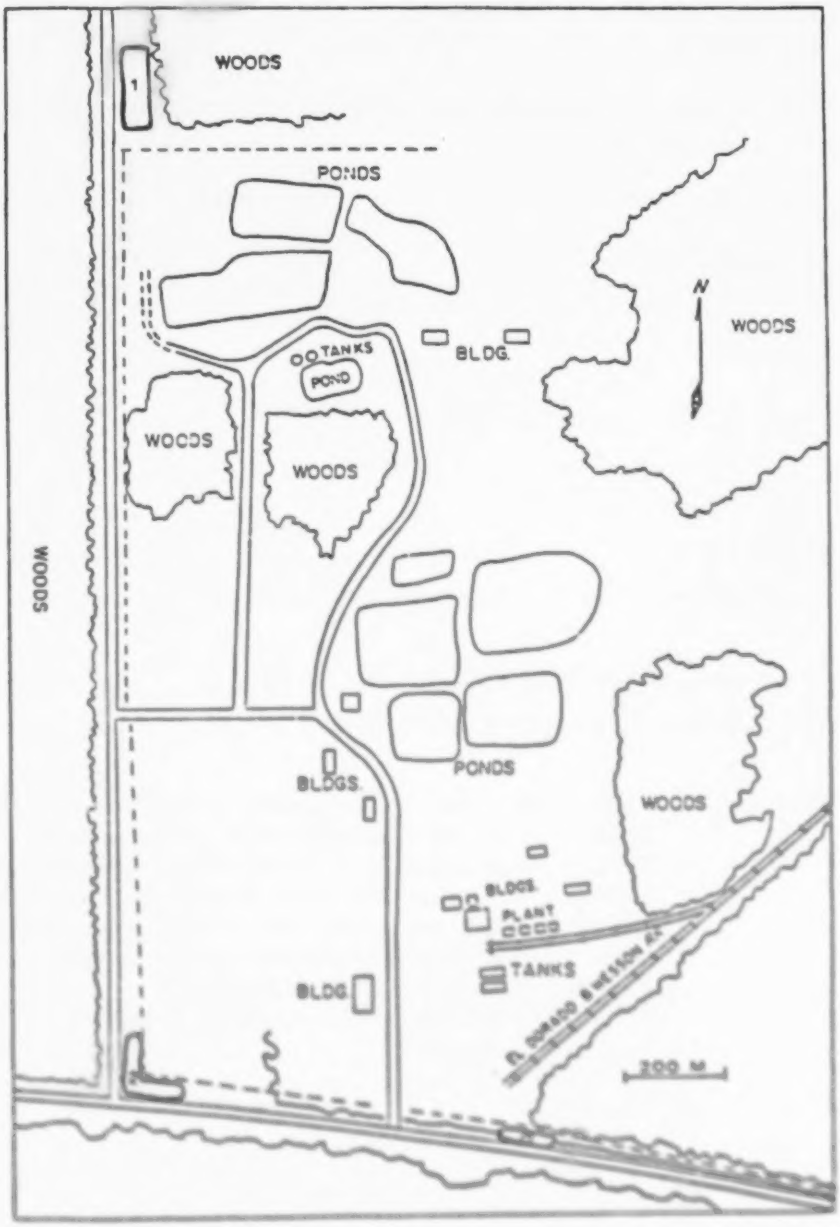
WOODS
1
PONDS
TANKS
POND
BLDG.
N
WOODS
WOODS
WOODS
WOODS
PONDS
BLDGS.
WOODS
BLDGS.
PLANT
TANKS
BLDG
EL DORADO & WESSON RR
200 M

Figure 4.6. Schematic map of Arkansas Chemical Incorp., El Dorado - sampling locations for F1 - 4/7/77.

4.2.1.2 Inorganics in Ambient Air

Chloride/Bromide and Chlorine/Bromine.--The results obtained by turbidimetric determination of total halide are given in Table 4.4. The site, period and cycle designation are given in the sampling protocols and the location on the schematic maps (Fig. 4.4).

Table 4.4. CONCENTRATIONS OF HALOGENS AND HALIDES IN AMBIENT AIR SURROUNDING ARKANSAS CHEMICAL INC.[a,b]

Species	Locations L1	 L2	 L3	 L4
Cl_2/Br_2[c]	<109	<92	<100	<61
Br_2[d]	-	238	-	28
Cl^-/Br^-[c]	<75	<61	69	49 ± 53
Br^-[d]	-	<19	-	<12

[a] Samples are from P1/C2.

[b] Values are in $\mu g/m^3$.

[c] By turbidity.

[d] By neutron activation analysis.

Arkansas Chemical Inc. showed only one detectable concentration of halide by turbidity at L4 (downwind of a group of ponds, see Fig. 4.4). Neutron activation analysis of that location indicated no bromide. A high bromide level was found at L2 which is inconsistent with the total halide determination. Cellulose filters used in the sampling cycle immediately following the impinger sampling cycle showed no detectable bromine.

Fluoride/Fluorine.--No fluoride or fluorine was detected in any of the samples in ambient air surrounding Arkansas Chemical Inc. The limits of detection are based upon the background levels observed in control solutions and are indicated by "less than" values. A detection limit of 0.02 ppm in the impinger solution was achieved for the volume of air sampled.

Acid Mist.--No titratable acid was detected in any samples (Table 4.5). Table 4.5 summarizes the upper limit of acid mist concentration in these samples. Again, they are represented as "less than values".

Table 4.5. ACID MIST IN AMBIENT AIR SURROUNDING ARKANSAS CHEMICAL INCORP. AS H_2SO_4[a]

		Locations			
Period	Cycle	L1	L2	L3	L4
P1	C3	-[b]	<30	-	<52

[a]Values in μg/m^3.

[b]Not determined.

Table 4.6. CONCENTRATION OF BROMINE IN BRINE SAMPLES

Site	Sample Type	μg Br/ml
Arkansas Chemical Incorp.	Front brine	6588.2
	Tail brine	418.2

4.2.1.3 Bromine and Brominated Organics in Brine

Neutron Activation Analysis.--Table 4.6 lists the concentrations of bromine (molecular plus halides) in front and tail brine samples. A 93% reduction of the bromine concentration was observed between front and tail brines. Significant quantities of bromine were detected in the tail brine samples; however, the technique of neutron activation does not distinguish whether the bromine is present as molecular bromine, bromide ion or brominated organics. Furthermore, the number of bromine atoms per molecule cannot be delineated. The importance of these results is primarily attributed to the presence of substantial quantities of "bromine" even after bromine extraction.

GC/MS/COMP Analysis for Volatile Organics.--The front brine from Arkansas Chemical Inc. was purged (Appendix A) to recover volatile brominated organics for subsequent identification by GC/MS/COMP and estimation of concentrations. The front brine sample from Arkansas Chemical Inc. (Fig. 4.7) contained benzene, dimethyldisulfide, toluene, thiacyclopentane, dithiopropane isomer, ethylbenzene, cyclooctatetraene, undecane and *n*-dodecane. The tail brine sample (Fig. 4.8) contained benzene, dimethyldisulfide, toluene and 1-chloro-2,3-dibromopropane (Fig. 4.9).

In Table 4.7 the concentrations of halogenated and other organics in brine samples from Arkansas Chemical Inc. are provided. In general the concentration of halogenated hydrocarbons did not appreciably increase after recovery of bromine from brine.

The above results represent the analysis of only a single sample in each case. For this reason the concentration of volatile organics in these samples may not be representative of the change in composition between front and tail brine. The results do, however, give an indication of the types of compounds which are present as volatile organics. It would be interesting in future studies to also include the examination of semi-volatile brominated organics in brine samples.

4.2.1.4 Organic Vapors in Ambient Air

Qualitative Analysis by High Resolution GC/MS/COMP.--Analysis was conducted according to the protocols given in Appendix A.

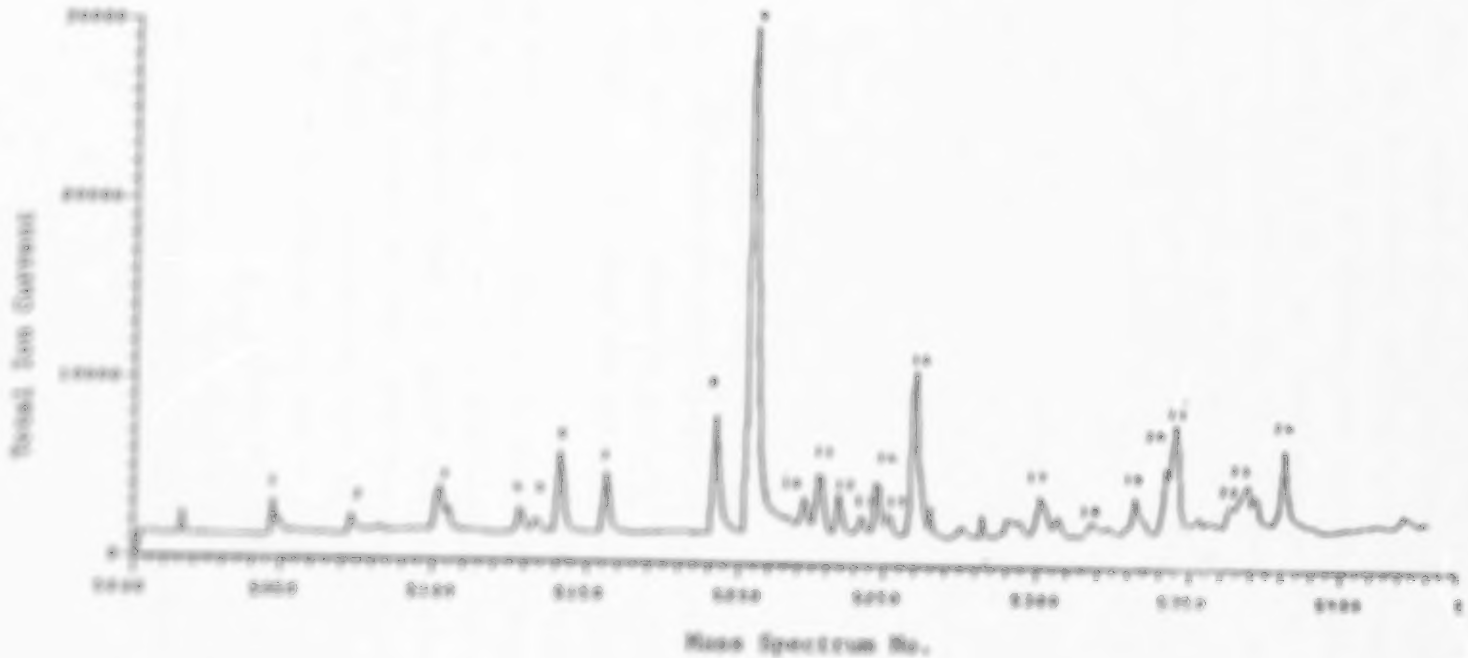

Figure 4.7. Total ion current profile of volatile organics in front brine from Arkansas Chemical Incorp. Peak No. 4 = hexafluorobenzene (s#), 5 = chloroform, 6 = perfluorotoluene (s#), 7 = benzene, 8 = dimethyldisulfide, 9 = toluene, 10 = thiacyclopentane, 12 = dichloropropane, 14 = ethylbenzene, 19 = cyclooctatetraene, 21 = n-undecane, 22 = $C_{12}H_{26}$ isomer, and 24 = n-dodecane.

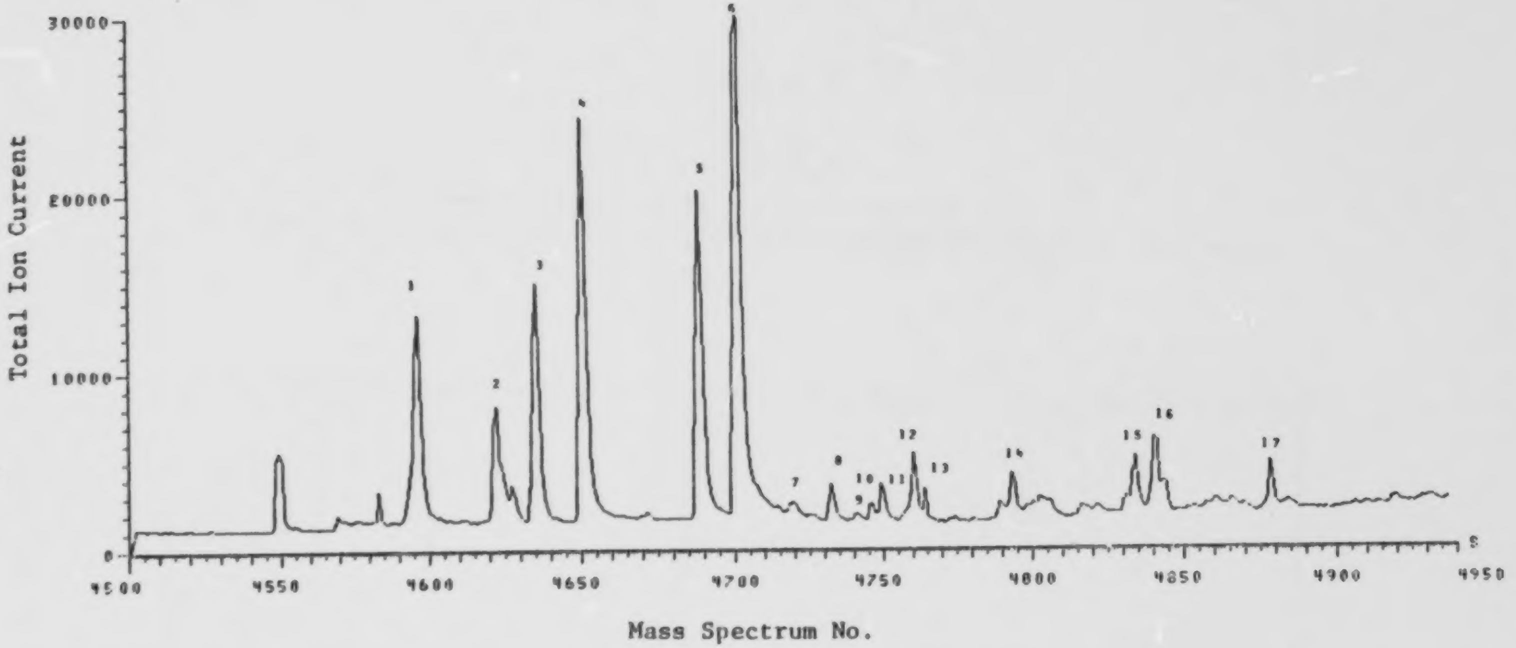

Figure 4.8. Total ion current profile of volatile organics in tail brine from Arkansas Chemical Incorp. Peak No. 2 = hexafluorobenzene (eS), 3 = perfluorotoluene (eS), 4 = benzene, 5 = dimethyldisulfide, 6 = toluene, and 15 = 1-chloro-2,3-dibromopropane.

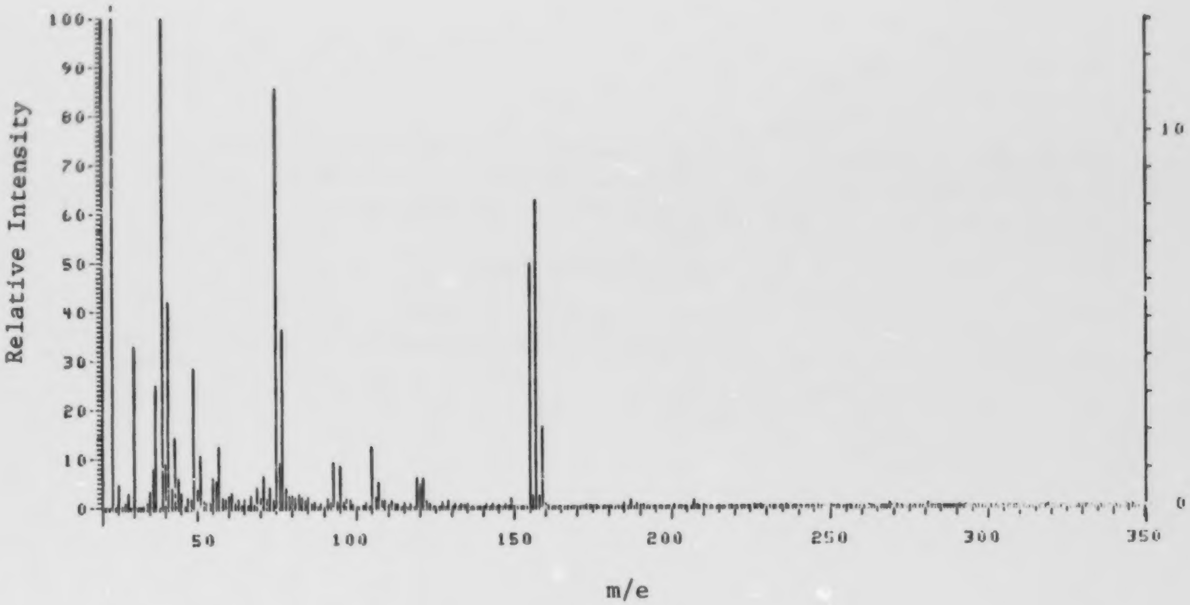

Figure 4.9. Mass spectrum of 1-chloro-2,3-dibromopropane in tail brine sample (ACI). Peak No. 15 in Figure 4.8.

Table 4.7. HALOGENATED AND OTHER ORGANICS IDENTIFIED AND QUANTITATED IN BRINE SAMPLES FROM ARKANSAS CHEMICAL INCORP.[a]

	Sample Type	
	Front Brine	Tail Brine
Dibromochloromethane	540	N.D.
1-Chloro-2,3-dibromopropane	40	56
Hexafluorobenzene (eS)[b]		-
Perfluorotoluene (eS)[b]		-
Ethylene dibromide		T(?)
Benzene	600	2,285
Toluene	10,000	3,200
Dimethyldisulfide	1,600	1,714
Thiacyclopentane	800	T
Dithiopropane isomer	1,600	1,400
Ethylbenzene	1,200	N.D.
n-Undecane	3,200	1,600
n-Dodecane	1,600	850
Cyclooctatetraene (tent.)	800	N.D.

[a] Concentrations are in ppt.

[b] eS = external standard, 200 ng.

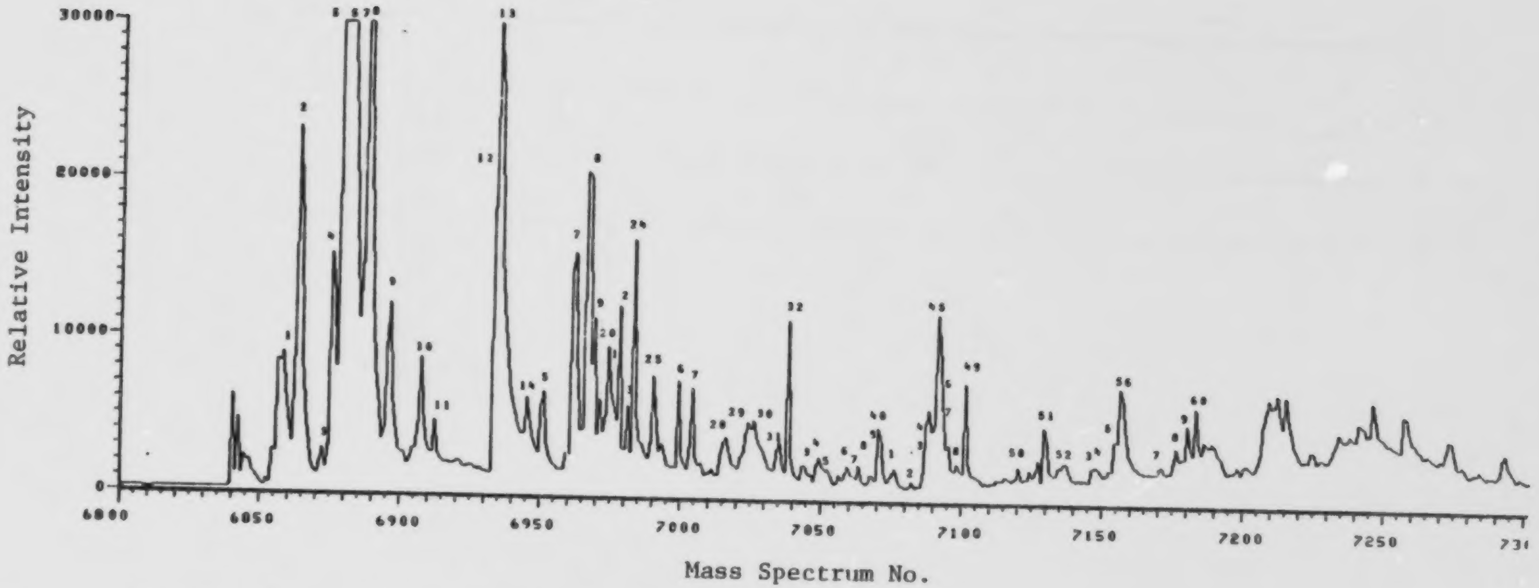

Figure 4.10. Total ion current profile of volatile ambient air pollutants from Arkansas Chemical Inc. site, El Dorado, Arkansas (P1/C1/L1).

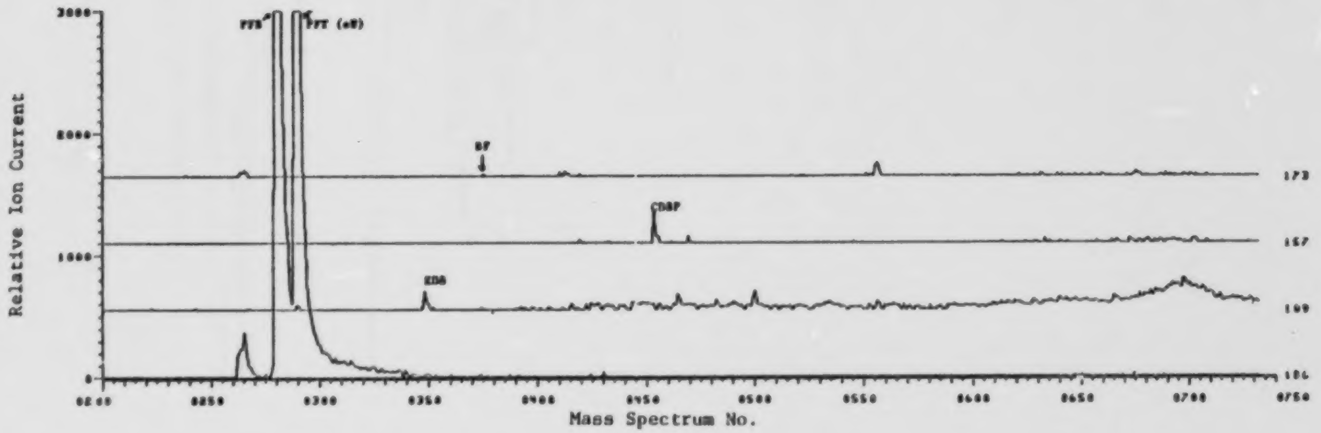

Figure 4.11. Ion chromatograms for ambient air sample from Arkansas Chemical Inc. site, El Dorado, Arkansas (P1/C1/L1). BF = bromoform, CDBP = 1-chloro-2,3-dibromopropane, EDB = ethylene dibromide.

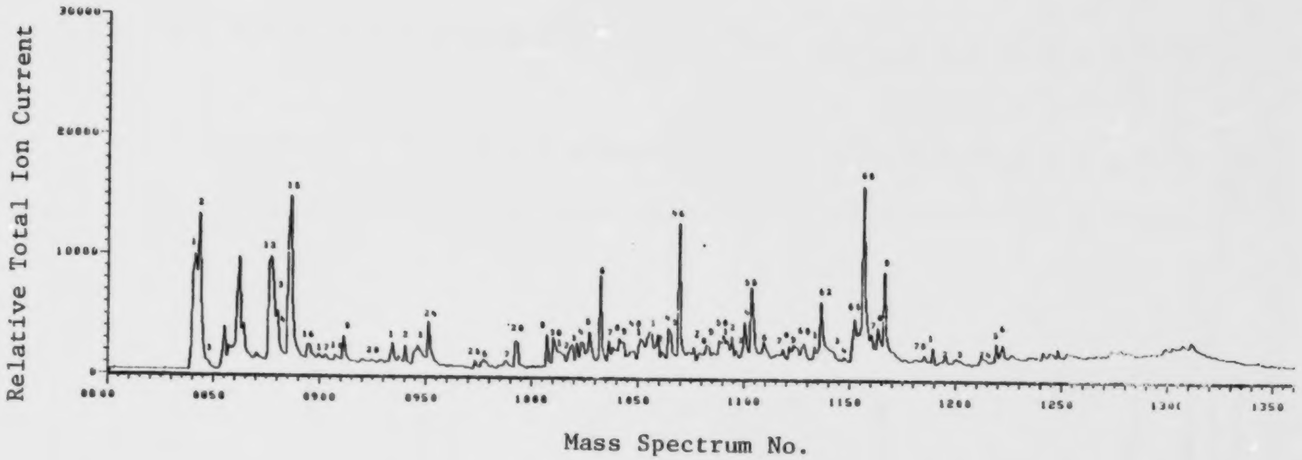

Figure 4.12. Total ion current profile of volatile ambient air pollutants from Arkansas Chemical Inc. site, El Dorado, Arkansas (P1/C1/L2).

Table 4.8. VOLATILE ORGANICS IDENTIFIED IN AMBIENT AIR FROM ARKANSAS CHEMICAL INC. SITE IN EL DORADO, ARKANSAS (P1/C1/L3)[a]

Chromatographic Peak No.	Elution Temperature (°C)	Compound
1	45	dichlorodifluoromethane
1A	46	acetaldehyde
2	47	trichlorofluoromethane
2A	48	acetone
2B	50	dichloromethane
3	51	freon 113 (BKG)
3A	53	isopropanol
3B	55	butenal isomer
3C	56	2-methylpentane
3D	57	3-methylpentane
3E	57	butanal (tent.)
4	58	hexafluorobenzene (eS)
4A	59	*n*-hexane
5	60	chloroform
6	63	perfluorotoluene (eS)
6A	64	methylcyclopentane
6B	65	1,1,1-trichloroethane
6C	67	benzene
7	68	carbon tetrachloride
7A	68	cyclohexane
7B	69	C_7H_{16} isomer
7C	70	methylbutanal isomer
8	73	*n*-pentanal
9	75	*n*-heptane
9A	79	C_7H_{14} isomer
9B	79	C_8H_{18} isomer
9C	80	methylcyclohexane
9D	84	4-methyl-2-pentanone
9E	85	methylpentanal isomer
10	87	toluene
10A	90	C_8H_{18} isomer
11	93	*n*-hexanal + 1,2-dibromoethane
11A	94	C_8H_{16} isomer
11B	96	silane compound (BKG)
12	96	*n*-octane
12A	97	tetrachloroethylene
12B	100	C_8H_{16} isomer
13	101	hexamethylcyclotrisiloxane (BKG)
13A	103	ethylcyclohexane
13B	104	C_9H_{20} isomer
14	106	ethylbenzene
15	108	*p*-xylene
16	109	C_9H_{20} isomer
16A	110	$C_{10}H_{22}$ isomer
17	111	styrene
18	112	2,2,4-trimethylheptane
18A	112	*m*-xylene
18B	113	*n*-heptanal
19	113	$C_{10}H_{22}$ isomer
19A	115	C_9H_{18} isomer
20	116	*n*-nonane
21	118	$C_{10}H_{20}$ isomer
21A	119	$C_{10}H_{22}$ isomer
22	120	dimethyl-ethylbenzene isomer
23	121	$C_{10}H_{22}$ isomer
24	122	$C_{10}H_{20}$ isomer
25	123	$C_{10}H_{22}$ isomer
25A	123	$C_{10}H_{16}$ isomer
25B	124	$C_{10}H_{22}$ isomer
26	125	benzaldehyde
26A	126	*n*-propylbenzene
27	127	*p*-ethyltoluene
28	128	$C_{10}H_{22}$ isomer
29	129	$C_{11}H_{24}$ isomer
30	130	$C_{11}H_{24}$ isomer
31	132	$C_{11}H_{24}$ isomer
32	133	C_3-alkyl benzene isomer
32A	134	$C_{10}H_{20}$ isomer
33	135	4-methyldecane
34	136	*n*-decane
35	137	$C_{11}H_{22}$ isomer
35A	138	$C_{10}H_{16}$ isomer
36	138	$C_{11}H_{24}$ isomer
37	139	C_4-alkyl benzene isomer
38	140	$C_{11}H_{24}$ isomer
39	141	$C_{10}H_{16}$ isomer
40	142	$C_{11}H_{24}$ isomer
41	144	$C_{11}H_{24}$ isomer
42	145	acetophenone
43	147	$C_{11}H_{24}$ isomer
44	149	C_4-alkyl benzene isomer

(continued)

Table 4.8 (cont'd)

Chromato-graphic Peak No.	Elution Temp. (°C)	Compound
44A	150	$C_{12}H_{24}$ isomer
45	152	n-nonanal
45A	153	$C_{11}H_{22}$ isomer
46	154	n-undecane
46A	157	C_4-alkyl benzene isomer
46B	157	$C_{12}H_{26}$ isomer
46C	159	$C_{12}H_{26}$ isomer
47	160	3-phenylpropenal
47A	163	C_5-alkyl benzene isomer
48	164	$C_{12}H_{26}$ isomer
48A	165	$C_{13}H_{28}$ isomer
49	169	n-decanal
49A	170	$C_{12}H_{24}$ isomer
50	171	n-dodecane
50A	174	$C_{13}H_{28}$ isomer
50B	184	$C_{13}H_{28}$ isomer
50C	188	$C_{13}H_{28}$ isomer

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[a] See Table 4.2 for sampling protocol.

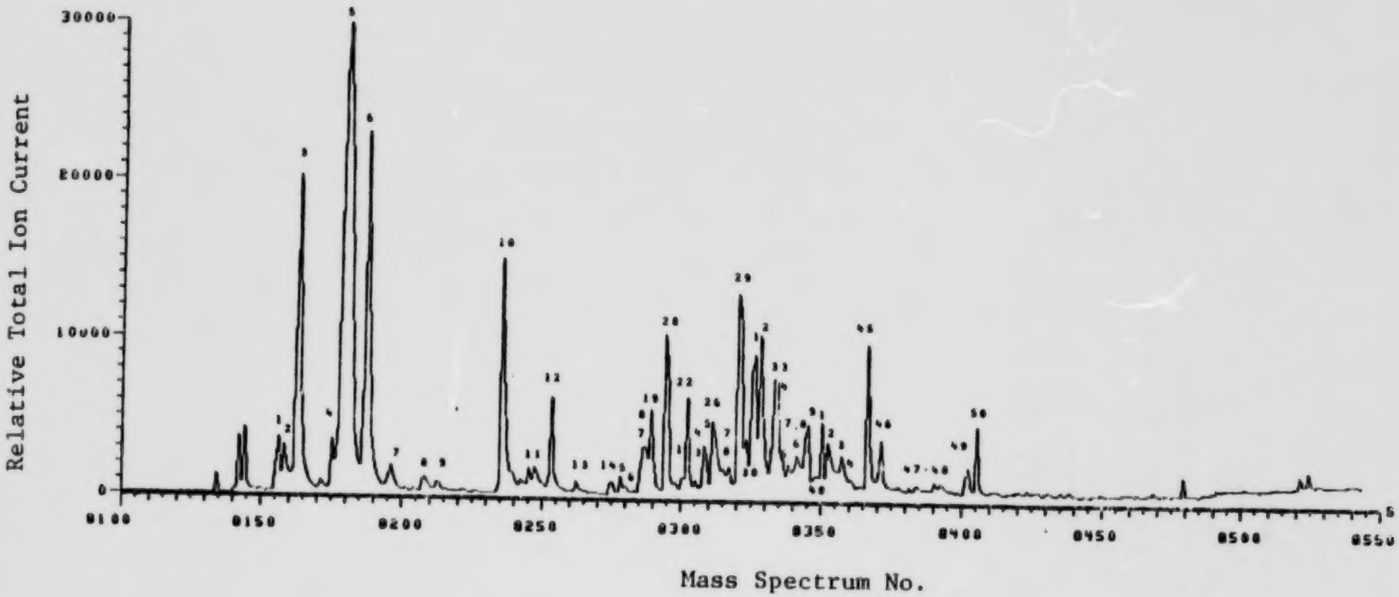


Figure 4.13. Total ion current profile of volatile ambient air pollutants from Arkansas Chemical Inc. site, El Dorado, Arkansas (P1/C1/L3).

Table 4.9. VOLATILE ORGANICS IDENTIFIED IN AMBIENT AIR FROM ARKANSAS CHEMICAL INC. SITE IN EL DORADO, ARKANSAS (P1/C1/L4)[a]

Chromatographic Peak No.	Elution Temperature (°C)	Compound
2	41	CO_2
2A	46	acetaldehyde
2B	47	difluorodibromomethane (tent.)
3	48	trichlorofluoromethane
3A	49	isopentane
4	50	acetone
4A	51	dichloromethane
5	52	freon 113 (BKG)
5A	53	isopropanol
5B	54	ter-butanol
5C	55	butenal
6	56	2-methylpentane
7	58	3-methylpentane
8	59	hexafluorobenzene (es)
9	60	n-hexane
9A	61	chloroform
10	64	methylcyclopentane
10A	65	perfluorotoluene (es)
10B	67	1,1,1-trichloroethane
11	68	benzene
11A	69	carbon tetrachloride
11B	70	cyclohexane
12	71	C_7H_{16} isomer
12A	71	methylbutanal isomer
12B	72	C_7H_{16} isomer
12C	73	hexamethyldisiloxane (BKG)
13	74	n-pentanal
14	76	n-heptane
14A	80	methylcyclohexane
14B	84	4-methyl-2-pentanone
14C	85	methylpentanal isomer
15	87	toluene
15A	92	C_8H_{16} isomer
16	93	1,2-dibromoethane
16A	93	n-hexanal
17	95	n-octane
17A	96	tetrachloroethylene
17B	96	C_8H_{16} isomer
17C	102	C_8H_{16} isomer
17D	103	C_9H_{20} isomer
18	106	ethylbenzene
18A	106	C_9H_{20} isomer
19	107	p-xylene
20	108	C_9H_{20} isomer
20A	100	C_9H_{20} isomer
21	111	styrene
22	112	$C_{10}H_{20}$ isomer
22A	112	m-xylene
23	113	n-heptanal
23A	113	$C_{10}H_{22}$ isomer
23B	114	C_9H_{18} isomer
24	115	n-nonane
24A	117	C_9H_{18} isomer
25	118	tetramethylhexane isomer
25A	119	C_3-alkyl benzene isomer
26	119	trimethylheptane isomer
27	120	dimethyl-ethylhexane isomer
28	121	$C_{10}H_{22}$ isomer
29	122	trimethylheptane isomer
29A	122	$C_{10}H_{16}$ isomer
30	123	benzaldehyde
31	125	$C_{10}H_{20}$ isomer
32	126	m-ethyltoluene
33	128	$C_{11}H_{24}$ isomer
34	129	$C_{11}H_{24}$ isomer
35	131	$C_{10}H_{16}$ isomer
36	132	$C_{10}H_{22}$ isomer
37	134	$C_{11}H_{24}$ isomer
38	134	n-decane + dichlorobenzene isomer
39	135	$C_{11}H_{24}$ isomer
40	136	$C_{10}H_{16}$ isomer
41	138	C_4-alkyl benzene isomer
41A	138	$C_{11}H_{24}$ isomer
41B	139	$C_{10}H_{16}$ isomer
42	140	$C_{11}H_{24}$ isomer
43	141	$C_{11}H_{24}$ isomer
44	142	$C_{11}H_{24}$ isomer
45	144	acetophenone
46	145	$C_{12}H_{26}$ isomer
46A	147	$C_{10}H_{12}$ isomer
47	148	$C_9H_{11}O$ isomer

(continued)

Table 4.9 (cont'd)

Chromato-graphic Peak No.	Elution Temp. (°C)	Compound
47A	149	$C_{10}H_{12}$ + $C_{11}H_{20}$ isomer
48	150	*n*-nonanal
48A	151	$C_{11}H_{22}$ isomer
49	152	*n*-undecane
49A	155	C_4-alkyl benzene isomer
49B	158	3-phenylpropenal
49C	161	dimethylphenol isomer
49D	165	dimethylphenol isomer
49E	167	*n*-decanal
50	168	$C_{12}H_{24}$ isomer
51	169	*n*-dodecane
51A	177	$C_{12}H_{24}$ isomer

[a] See Table 4.2 for sampling protocol.

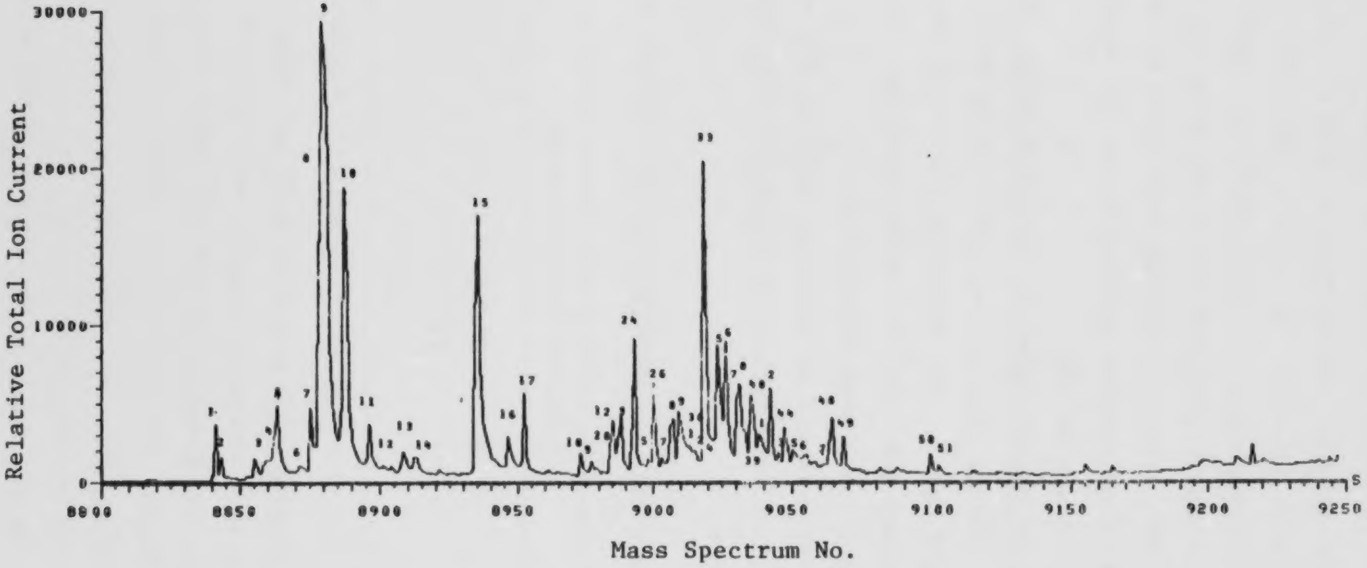


Figure 4.14. Total ion current profile of volatile ambient air pollutants from Arkansas Chemical Inc. site, El Dorado, Arkansas (P1/C1/L4).

Quantification of Halogenated Hydrocarbons.--The identified halogenated hydrocarbons were quantified (Section F, Appendix A). Table 4.11 presents the levels of halogenated hydrocarbon in samples taken near the spent brine pond on the Arkansas Chemical Inc. site. The highest level observed was 133 ng/m^3 (1,2-dibromoethane). This sample was taken at L4 and it actually represented an upwind sample from the brine pond and the bromine extraction facility. For this reason it was believed that the brominated compound had been transported from another facility since the analysis of spent brine indicated only a trace of EDB.

Estimation of Methyl Chloride, Methyl Bromide, Vinyl Chloride and Vinyl Bromide.--Methyl chloride was detected by GC/EC in one sample (P1/C3/L1) at a level of 200 μg/m^3. The detection limit was about 200 μg/m^3 for methyl chloride and 120 μg/m^3 for methyl bromide. No other halogenated species (of these four) were detected at ACI.

Ethylene.--The levels of ethylene found at ACI are given in Table 4.12. These values were typical background levels observed in most samples taken in this area.

Table 4.12. CONCENTRATIONS OF ETHYLENE IN AMBIENT AIR[a]

Site	Period/Cycle/Location	ppm
ACI	P1/C3/L1	0.76 ± 0.16
	P1/C3/L2	0.85 ± 0.15
	P1/C3/L5	0.76 ± 0.16

[a] See Table 4.2 for sampling protocol and Fig. 4.4 for locations.

4.2.1.5 Brominated Organics in Soil and Water

All of the soil and water samples were screened by the VOA method (Appendix A) for the presence of EDB and other volatile brominated compounds, and none were found. One of the soil samples [P1/C1/L1 (April 4, 1977)] was selected for analysis for semi-volatile brominated organics. The results are given in Table 4.13.

The spectrum of Tetrabrom obtained from the soil sample P1/C1/L1 is shown in Figure 4.15.

Table 4.11. HALOGENATED HYDROCARBONS IDENTIFIED AND QUANTITATED IN AMBIENT AIR SURROUNDING ARKANSAS CHEMICAL INCORP., EL DORADO, AK

Period/Cycle/Location[a]	Allyl bromide	Bromoform	1 or 2-Bromopropane	1-Chloro-2,3-Dibromopropane	1,2-Ethylene dibromide	Difluorodibromomethane
P1/C1/L1	70	T[b]	-	1.87	3.10 + 0.8	-
L2	T	-[c]	-	-	5.30	-
L3	29.7	-	5.5	-	81	-
L4	-	-	6.7	-	133	T

[a] Refer to Table 4.2 for sampling protocol, values are in ng/m^3.

[b] T = trace detected.

[c] - = not detected.

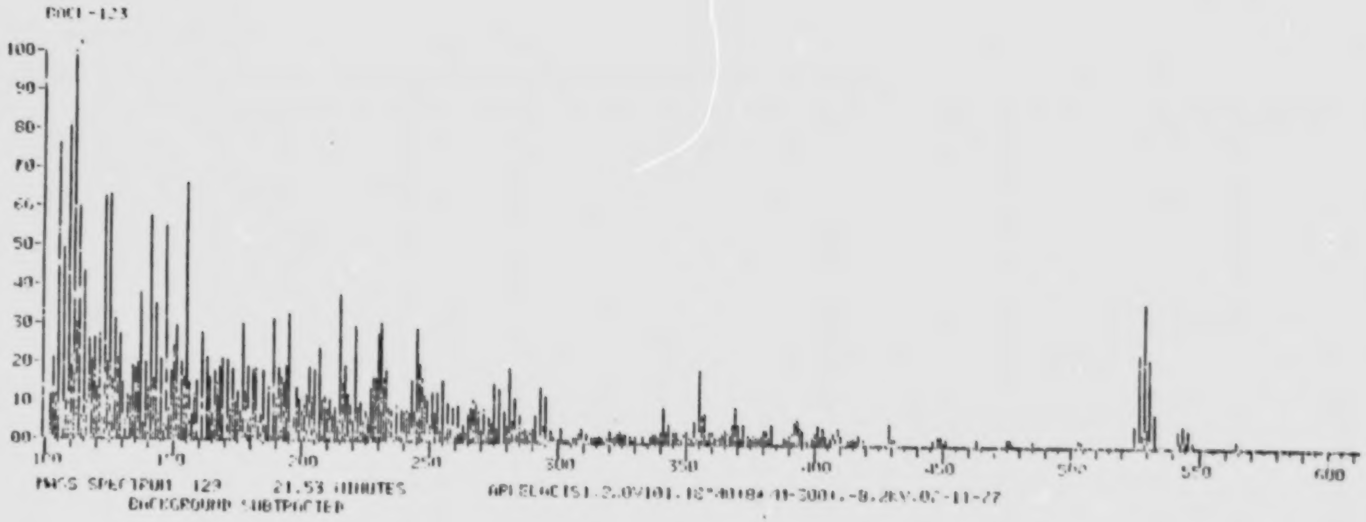


Figure 4.15. Mass spectrum of Tetrabrom in soil sample P1/C1/L1.

Table 4.13. ANALYSIS OF A SOIL SAMPLE COLLECTED NEAR ARKANSAS CHEMICALS, INCORPORATED, EL DORADO, AK

Period/Cycle/Location	EDB (µg/k)	Decabrom (g/k)	Tetrabrom (µg/kg)
P1/C1/L1	ND	260[a,b]	4,100[a,c]

[a] Quantitated by GC/MS/COMP with multiple ion detection (MID).

[b] Confirmed by GC/MS/COMP-MID using ion intensity ratios; m/e 800:960 was 3.0 for standards and 2.7 for the sample.

[c] Confirmed by GC/MS/COMP in full scan mode.

4.2.2 Great Lakes Chemical Corporation

4.2.2.1 Sampling

The sampling protocol and sample descriptions for Great Lakes Chemical Corporation are given in Table 4.14. The corresponding Figures 4.16-4.18 designate the sampling locations for September 22-24, 1976. The sampling protocols for April 7, 22, and 29 and May 17, 1977 are given in Table 4.15 and their locations in Figures 4.19 and 4.20.

4.2.2.2 Survey of Chemicals on Glass Fiber and Cellulose Filters

Scanning Electron Microscopy (SEM) and Electron Microprobe (EM) Analysis.--Samples were collected at Great Lakes Chemical Corp. by the State of Arkansas Air Pollution Control Division using Hi-Vol samplers. Glass fiber filters (GFF) and cellulose filters (CF) were sampled in parallel. Each site was sampled for three 24 hour periods. One period from each site has been analyzed by SEM and EM. Both types of filter material were examined. Sufficient sample was concentrated on the surface of the GFF to permit direct analysis without the usual carbon-coating to prevent charge buildup on the sample.

Initially, an examination for the presence of bromine and its subsequent mapping was performed. In Figure 4.21 the EM spectrum shown is expanded for the greatest sensitivity in the bromine region. Traces were detectable in both samples when compared to the background in Figure 4.22. However, these traces are insufficient to produce an elemental map.

Table 4.14. SAMPLING PROTOCOL FOR GREAT LAKES CHEMICAL CORPORATION, HIGHWAY 15, EL DORADO, ARKANSAS

						Meteorological Conditions			
Period	Cycle	Location	Sampling Time	Sampling Volume (ℓ)	Type of Sample	T (°C)	% RH	Wind Dir./ Speed (kmph)	Other
9/22/76 P1	C1	L1	1026-1234	109	HHC^a	24-26	51-46	130/3-230/3-6	Clear
		L2	1026-1234	122	HHC^a				
		L3	1026-1234	140	HHC^a	26		variable/light	Clear, slight odor of Br$_2$
		L4	1026-1233	100	HHC^a	24	51		Clear, odor of bromobenzene Brine Pit-heavy odor
	C2	L5 (ELV)	1010-1702	-	HHC^c	26			
		L2 (ELV)	945-1702	-	HHC^c				
		L2	945-1702	-	HHC^b				
		L3	1026-1700	-	HHC^b	26		calm	Clear, odor of Br$_2$
		L4	1026-1602	-	HHC^b	28-30		calm	
	C3	L1	1238-1337	46.7	F, CBN, CBD	27		230/3-6	
		L2	1236-1336	54.6	F, CBN, CBD				
		L3	1236-1336	48.1	F, CBN, CBD	28			Clear, slight odor of Br$_2$
		L4	1233-1336	77.8	F, CBN, CBD			shifted to South	
	C4	L1	1340-1450	123	AM			230/3-6	No drift
		L2	1337-1451	137	AM				
		L3	1337-1451	103	AM				
		L4	1340-1453	125	AM	28			Clear
		L5	1130	1	TED				
		L6	1138	1	TED				
		L7	1143	1	TED				

(continued)

Table 4.14 (cont'd)

Period	Cycle	Location	Sampling Time	Sampling Volume (ℓ)	Type of Sample	Meteorological Conditions			
						T (°C)	% RH	Wind Dir./ Speed (kmbh)	Other
9/22/76 P1		L6	1130	0.28	VAC				
		L8	1143	0.28	VAC				
9/22/76 P2	C1	L1	1553-1802	116	HHC^a	22	65	South/3	Clear
		L2	1548-1608	96	HHC^a				
		L3	1600-1831	160	HHC^a	33-30	38	clear	Clear, odor of brine steam
		L4	1549-1823	191	HHC^a			270°/5-5KTS	Clear, light Br$_2$ odor
9/22,23/76	C2	Parkers Chapel Water Tower	1730-1030	-	HHC^c				
	C3	L1	1813-1913	36.8	F, CBN, CBD				
		L2	1827-1932	73.6	F, CBN, CBD				
		L3	1803-1916	59.4	F, CBN, CBD	30		240°/5-8	
	C4	L5	1930	-	VAC				
9/24/76 P3	C1	L1	1200-1420	229	HHC^a	29	38	North/8	
		L2	1200-1420	178	HHC^a				
		L3 (ELV)	1200-1420	205	HHC^e				Clear, odor phenol, slight Br$_2$
		L4	1200-1420	216	HHC^f				Upset at 1304-1309
	C2	L3 (ELV)	1740-948	-	HHC^d			30°/3-10	
		L5 (ELV)	1745-945	-	HHC^d			180°/3-11	

(continued)

Table 4.14 (cont'd)

Period	Cycle	Location	Sampling Time	Sampling Volume (ℓ)	Type of Sample	Meteorological Conditions T (°C)	% RH	Wind Dir./ Speed (kmph)	Other
9/24/76 P3	C3	L4	1018-1818	-	HHC[d]			30°/3-10	
		L6 (ELV)	1145-1824	-	HHC[c]				
	C4	L7	1428-1536	62	F, CBN, CBD	28-29	38-42	ENE-NNE/8-13	Clear, visible Br_2 plume SE, Black smoke NE, odor of H_2S
		L2	1430-1536	59	F, CBN, CBD				Clear, strong odor of Br_2 and phenol
		L3	1430-1536	85	F, CBN, CBD				
		L4	1430-1536	74	F, CBN, CBD				
	C5	L7	1540-1652	119	AM				
		L2	1540-1652	147	AM				
		L3	1542-1652	110	AM				Clear, slight odor of Br_2
		L4	1540-1652	143	AM				
	C6	L7	1657-1806	51	F, CBN, CBD				
		L2	1657-1758	54	F, CBN, CBD				
		L3	1659-1706	64	F, CBN, CBD				Odor of phenol
		L4	1657-1803	68	F, CBN, CBD				

[a] Nutech Model 220 sampler 3-6 ft elevation

[b] DuPont sampler 3-6 ft elevation

[c] DuPont sampler 15-18 ft elevation

[d] Overnight sampling

[e] Sampling done on top of 3 story tower

[f] Sampling done on top of Tank

Locations shown in Figures 7, 8, and 9.

Key to Sample Type:

HHC - Halogenated Hydrocarbon
F - Fluorine and Fluoride
CBN - Bromine and Bromide
CBD - Chlorine and Chloride
AM - Acid Mist
TED - Tedlar bag
VAC - Aluminum Vacuum Can

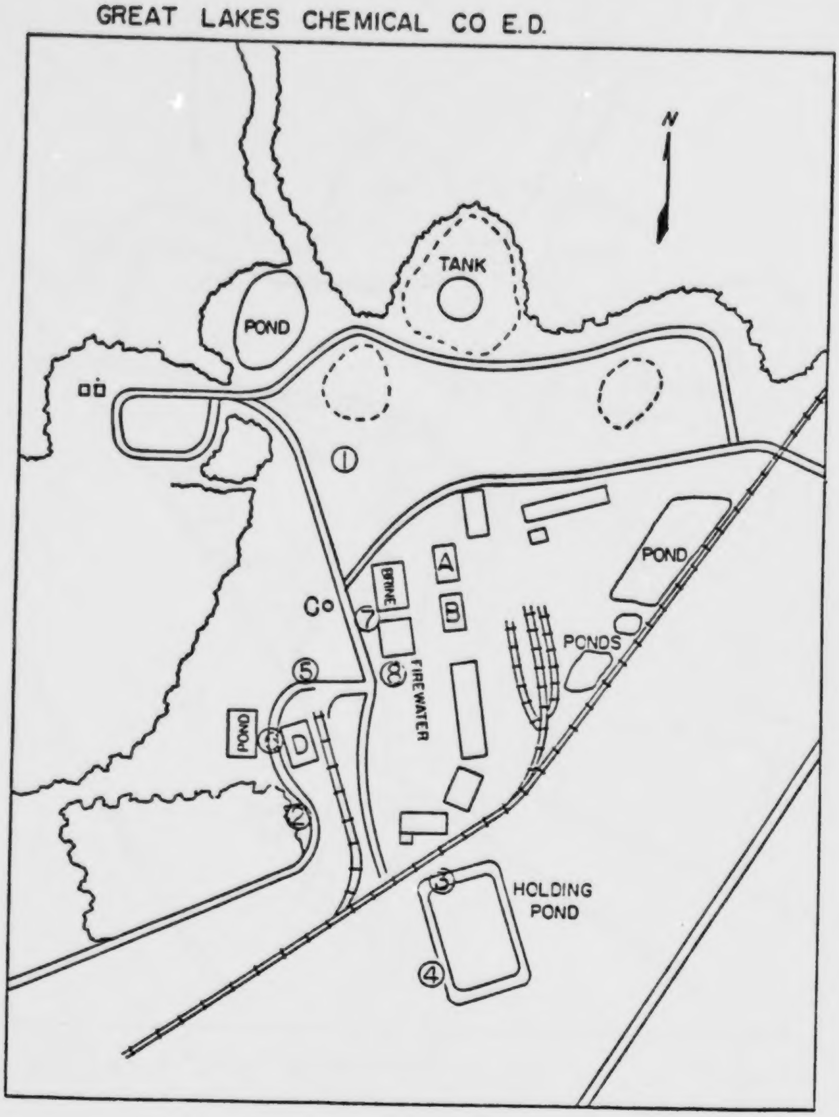

GREAT LAKES CHEMICAL CO E.D.
N
TANK
POND
①
BRINE
A
B
C
⑦
⑤
⑧
FIREWATER
POND
⑥
D
②
POND
PONDS
③
HOLDING POND
④

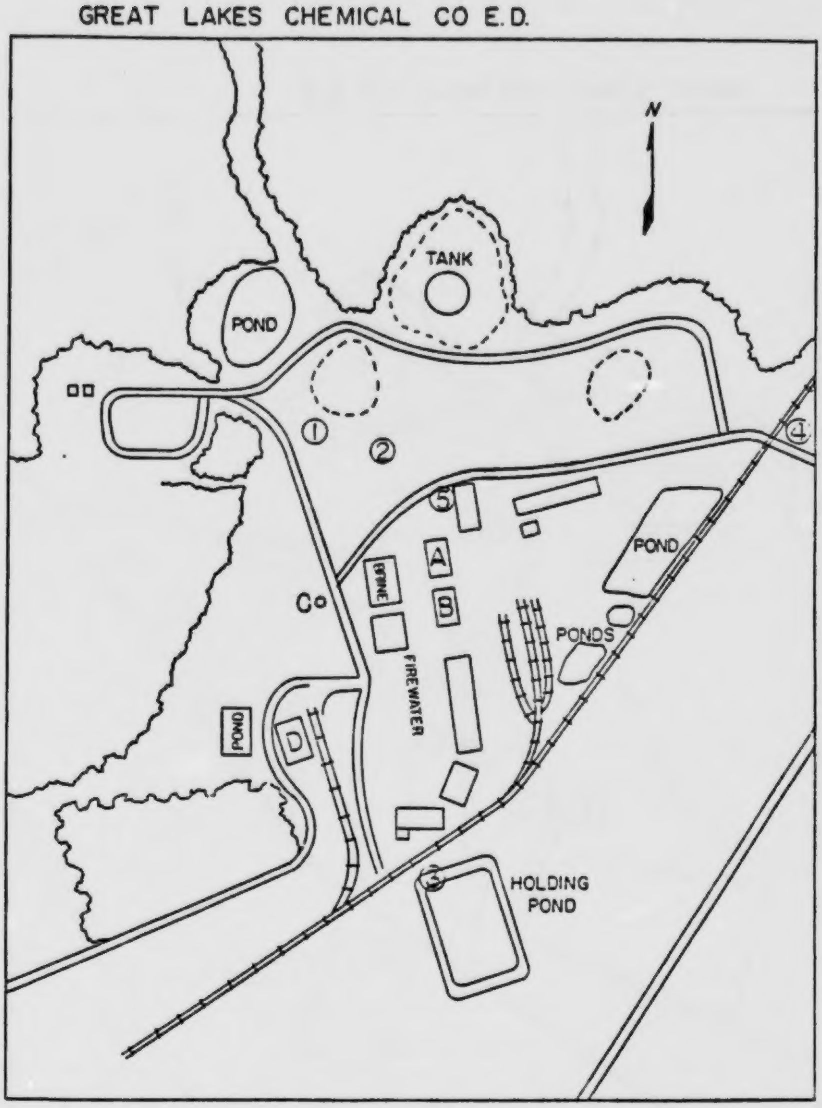
Figure 4.16. Schematic map of Great Lakes Chemical Corp., El Dorado - sampling locations for P1 - 9/22/76

A - EDB facility

B - Br_2 facility

C - H_2S stripper

D - Tetrabrom facility


GREAT LAKES CHEMICAL CO E.D.
N
TANK
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⑤
A
B
BRINE
C○
POND
PONDS
FIREWATER
POND
D
③
HOLDING POND

APPROX. SCALE 1 cm = 110 m

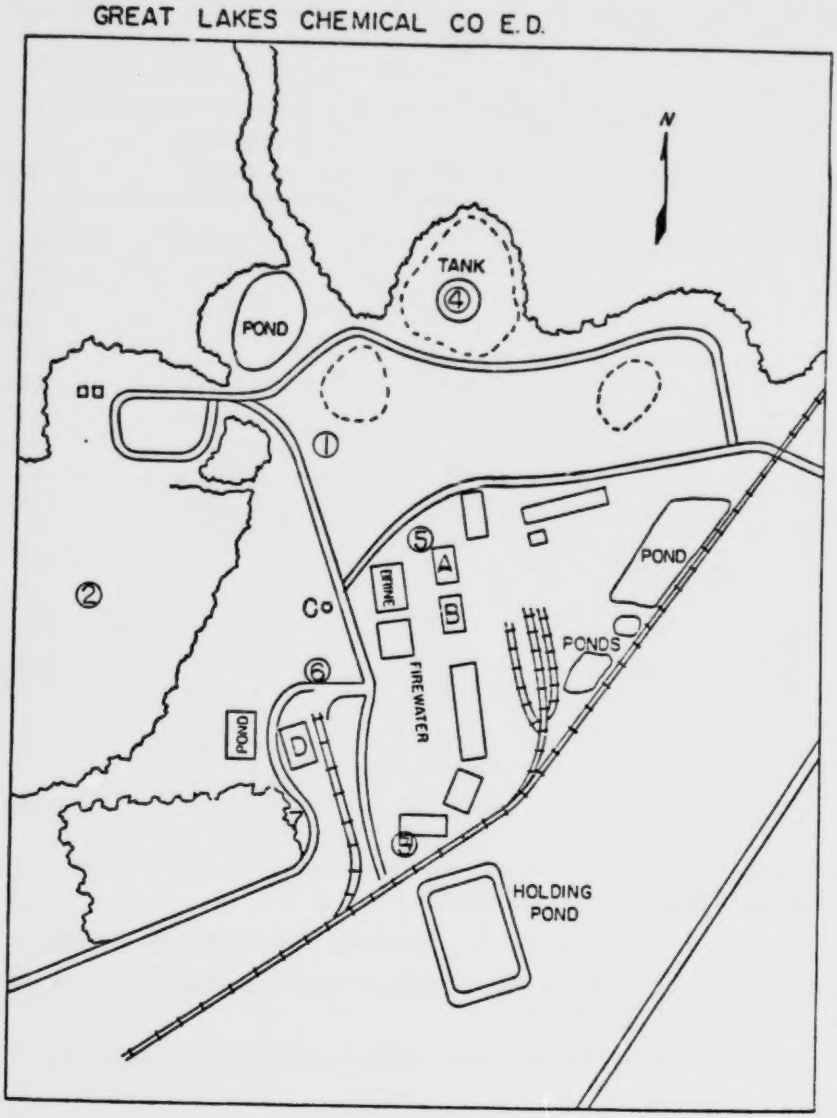
Figure 4.17. Schematic map of Great Lakes Chemical Corp., El Dorado - sampling locations for P2 - 9/22/76.

A - EDB facility

B - Br_2 facility

C = H_2S facility

D = Tetrabrom facility


GREAT LAKES CHEMICAL CO E.D.
N
TANK
④
POND
①
②
⑤
A
B
C
BRINE
POND
PONDS
⑥
FIREWATER
POND
D
⑤
HOLDING POND

APPROX. SCALE 1 cm = 110 m

Figure 4.18. Schematic map of Great Lakes Chemical Corp., El Dorado - sampling locations for P3 - 9/24/76.

A - EDB facility

B - Br_2 facility

C - H_2S stripper

D - Tetrabrom facility

Table 4.15. SAMPLING PROTOCOL FOR GREAT LAKES CORPORATION, EL DORADO, ARKANSAS

Period	Cycle	Location	Sample Size	Type of Sample
P1 4/7/77	C1	L1	2 core[a]	SHHC-V
			2 core	SHHC-SV
			1 ℓ	WHHC-V/SV[b]
				VHHC-V[c]
				VHHC-SV[b]
		L2	2 core	SHHC-V
			2 core	SHHC-SV
			1 ℓ	WHHC-V/SV[d]
		L3	2 core	SHHC-V
			2 core	SHHC-SV
		L4	--	VHHC-V
				VHHC-SV
P2 4/22/77	C1	L1		SEHHC-V/SV
		L2		SCHHC-V/SV
		L3		SEHHC-V/SV
		L4		SCHHC-V/SV
P3 4/29/77		Parkers Chapel	1 ℓ	MHHC-V/SV
P4 5/17/77	C1	Parkers Chapel		VHHC-V/SV[e]

[a] Core ∿5 cm diameter, 13 cm depth.

[b] ∿2/3 m wide, ∿1 cm deep in dry weather (no rain for 1 week).

[c] Needles stripped from 40 cm of pine bough sampled at ∿5 m above ground from trees showing damage.

[d] Stream ∿30 cm wide, ∿5 cm deep in dry weather (no rain for 1 week).

[e] Apples.

Key to sample type:
SHHC - soil for halogenated hydrocarbons
WHHC - water for halogenated hydrocarbons
VHHC - vegetation for halogenated hydrocarbons
SEHHC - sediment for halogenated hydrocarbons
SCHHC - scum on water for halogenated hydrocarbons
MHHC - milk for halogenated hydrocarbons
V - for volatile organic analysis
SV - for semi-volatile organic analysis

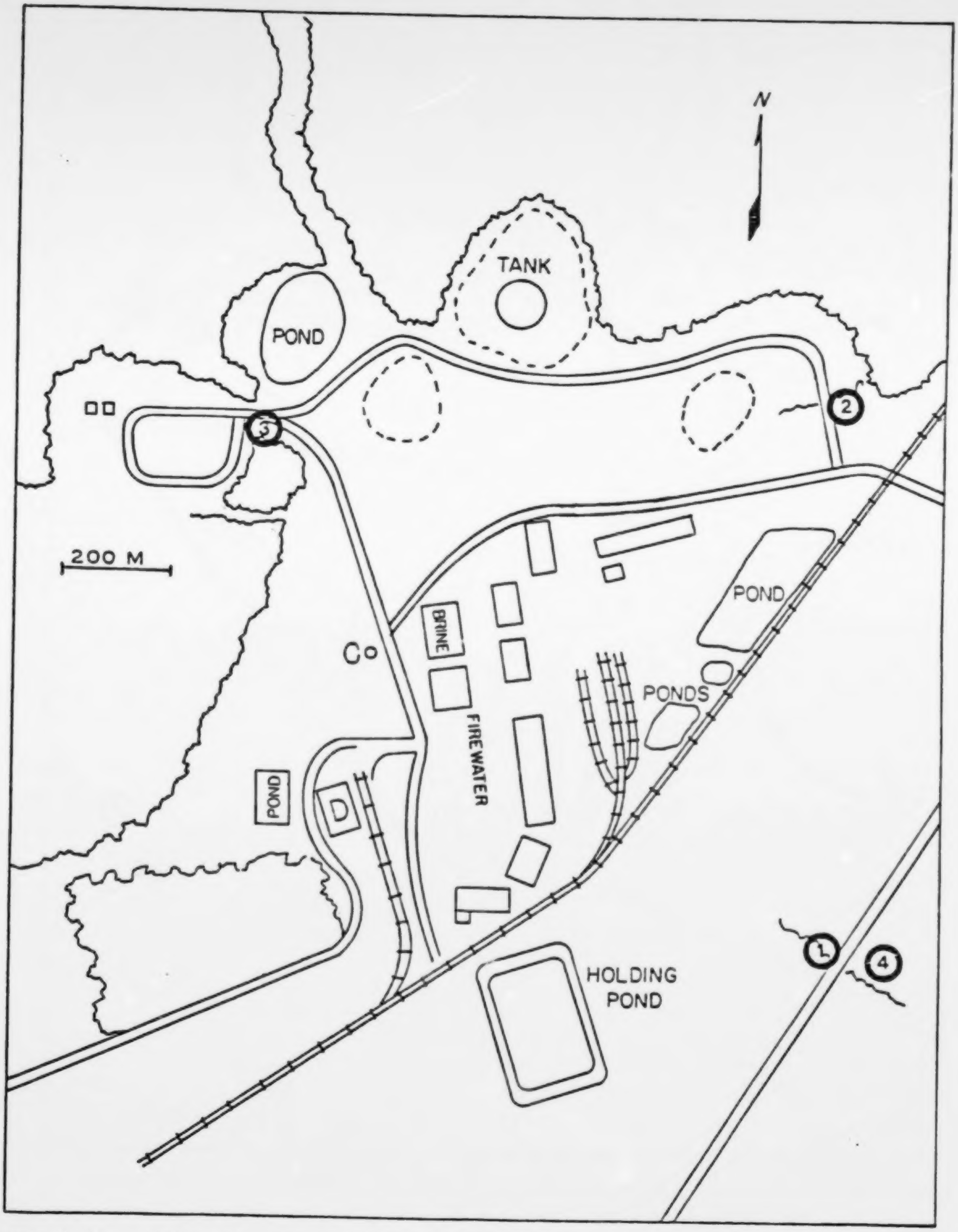

N
TANK
POND
2
3
200 M
POND
BRINE
Co
PONDS
FIREWATER
POND
D
HOLDING POND
1
4

Figure 4.19. Schematic map of Great Lakes Chemical Corporation, El Dorado - sampling locations for P1 - 4/7/77.

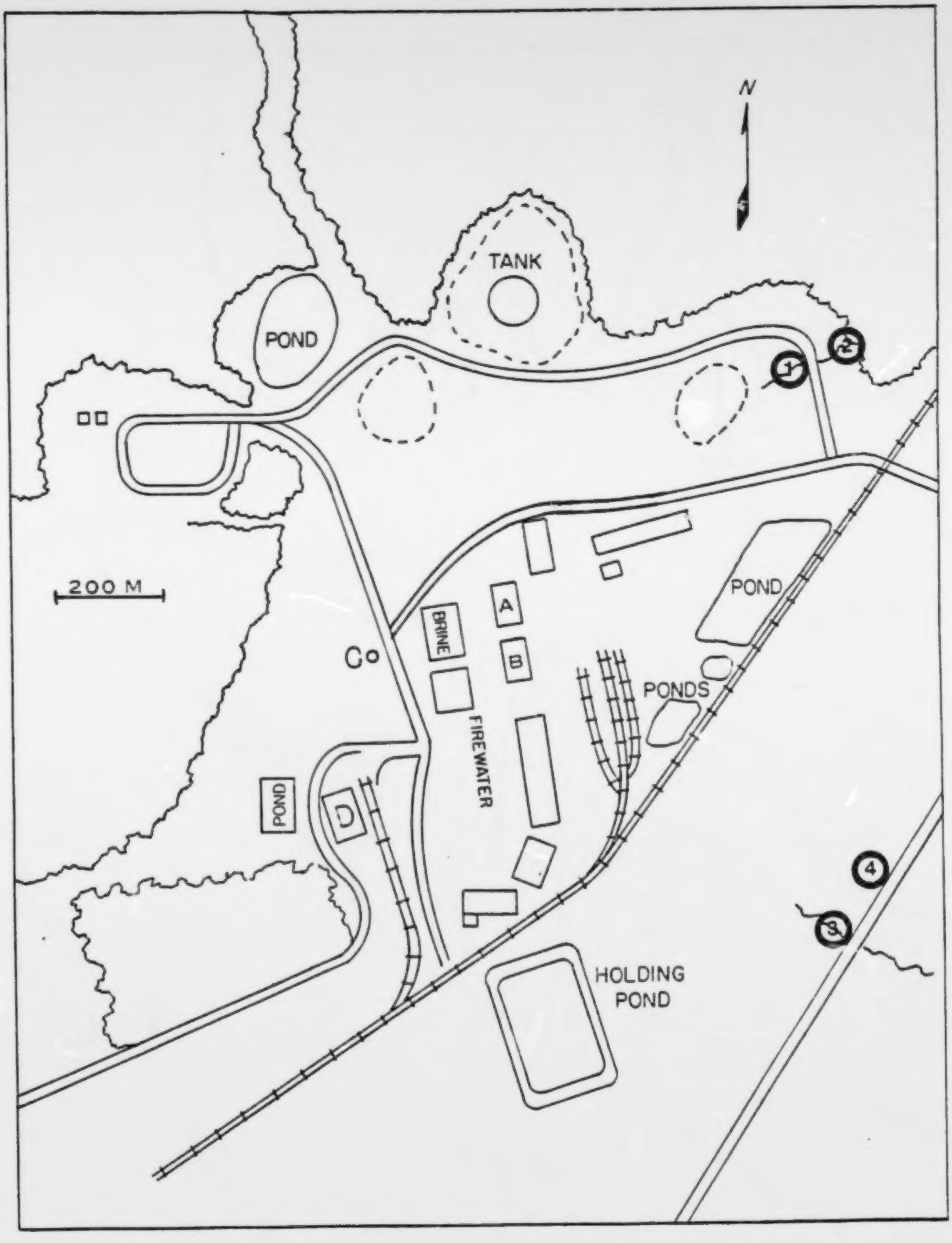

N
TANK
POND
200 M
A
B
BRINE
Co
FIREWATER
POND
PONDS
POND
D
HOLDING POND
1
2
3
4

Figure 4.20. Schematic map of Great Lakes Chemical Corporation, El Dorado - sampling locations for P2 - 4/22/77.

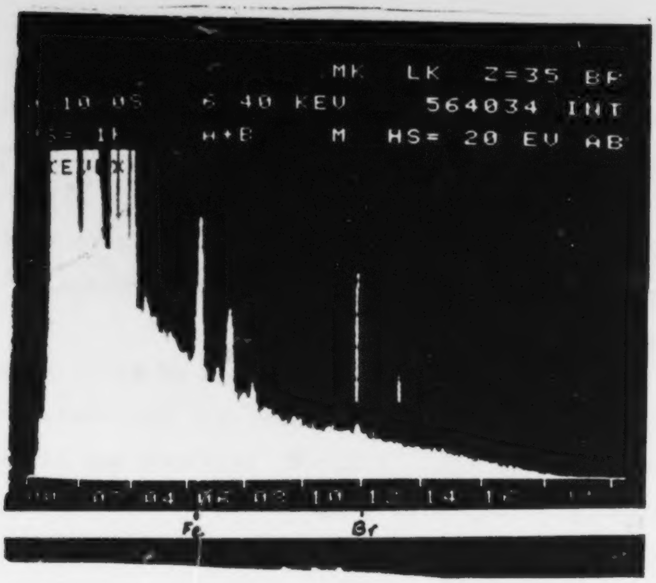


Figure 4.21. Great Lakes Chemical Corporation, El Dorado, Arkansas on 12/17/76 - 12/18/76. Volume sampled 2,733.6 m^3 air.

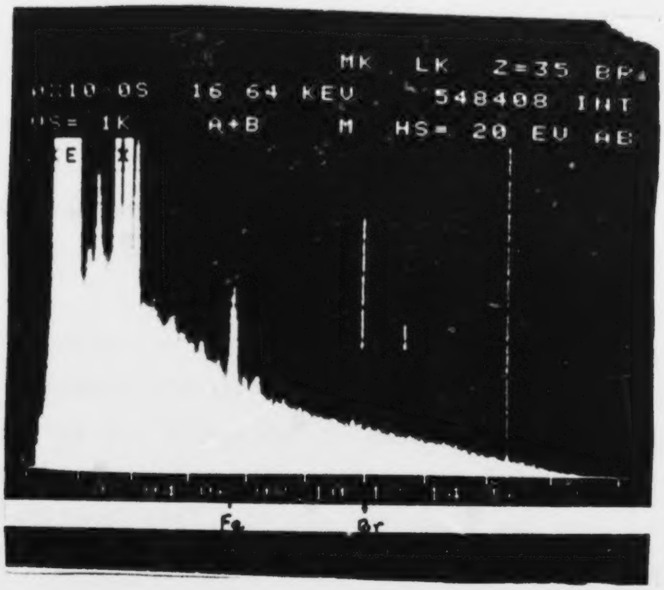


Figure 4.22. Electron microprobe spectrum of blank glass fiber filter.

An inspection of the total spectrum of the GFF from Great Lakes Chemical Corp. (Fig. 4.23a) reveals several other elements which were significantly above background (that is, chlorine, aluminum, and iron). The amount of sulfur is especially high compared to chlorine. Electron microprobe maps of chlorine, sulfur, aluminum, and silicon are shown in Figures 4.23-4.25 along with the SEM maps of the region (Fig. 4.23). There is some degree of coincidence of aluminum and silicon indicating an aluminum silicate particulate is probably present.

In general, this analysis surveys the types of particulate which were present. Since elements of low atomic number are not observed, carbon and its compounds escape observation. Indirect evidence may be obtained for halogenated organics by eliminating possible counterions. Such was the case of a particulate found on a GFF used during halogenated hydrocarbon sampling (P1/C1/L4). The spectrum, SEM and maps for chlorine, sodium, potassium, calcium and magnesium are shown in Figures 4.26-4.29. There were relatively low amounts of counterions as compared to the chlorine. Calcium is at background. Magnesium shows the greatest intensity, but even so it is weak compared to chlorine.

Neutron Activation Analysis.--A segment of each filter was submitted to neutron activation analysis. The segment was 2 x 2 cm cut from the medium fold with the distal edge of the segment 3 cm from the filter edge. The results of the neutron activation analysis are shown in Table 4.16. The highest concentration of bromine (20.2 $\mu g/m^3$) was detected in a sample taken on December 17, 1976. Also, this represented the period for the highest chlorine value (1.7 $\mu g/m^3$) observed during the three day sampling period.

Brominated Organics.--The filters above were extracted as described in Appendix A and analyzed by thin layer chromatography-scanning densitometry for Decabrom. The results are listed on Table 4.17. A second extraction of the GFF from 12/18/76 was rechromatographed and the band corresponding to Decabrom scraped from the plate and eluted. This fraction was submitted to direct probe MS analysis. The spectrum is shown in Figure 4.30. A spectrum of authentic Decabrom is shown in Figure 4.31. Large amounts of a yellow material remained near the origin on the GLC plate. This material

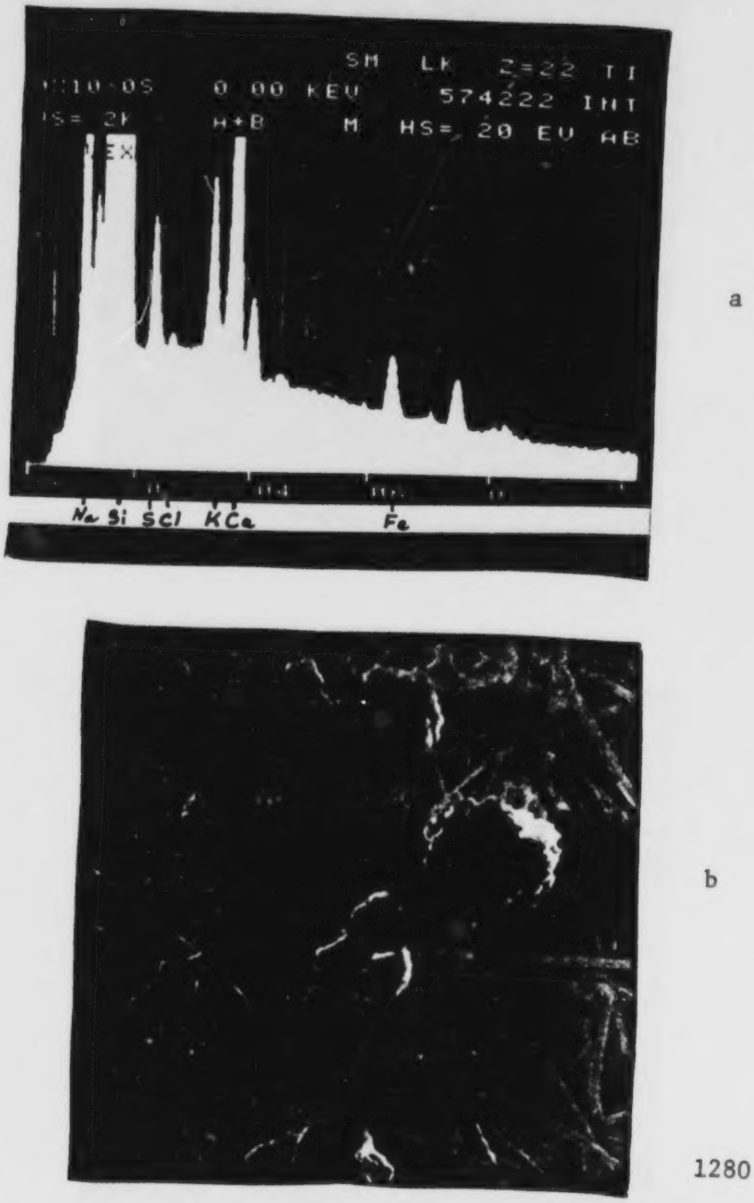


Figure 4.23. Electron microprobe spectrum (a) and scanning electron micrograph (b) of a region on an air sample collected on glass fiber filter. Sample Volume: 2,733.6 m^3; Location: Great Lakes Chemical Corporation, El Dorado, Arkansas. Collected 12/17/76 - 12/18/76.

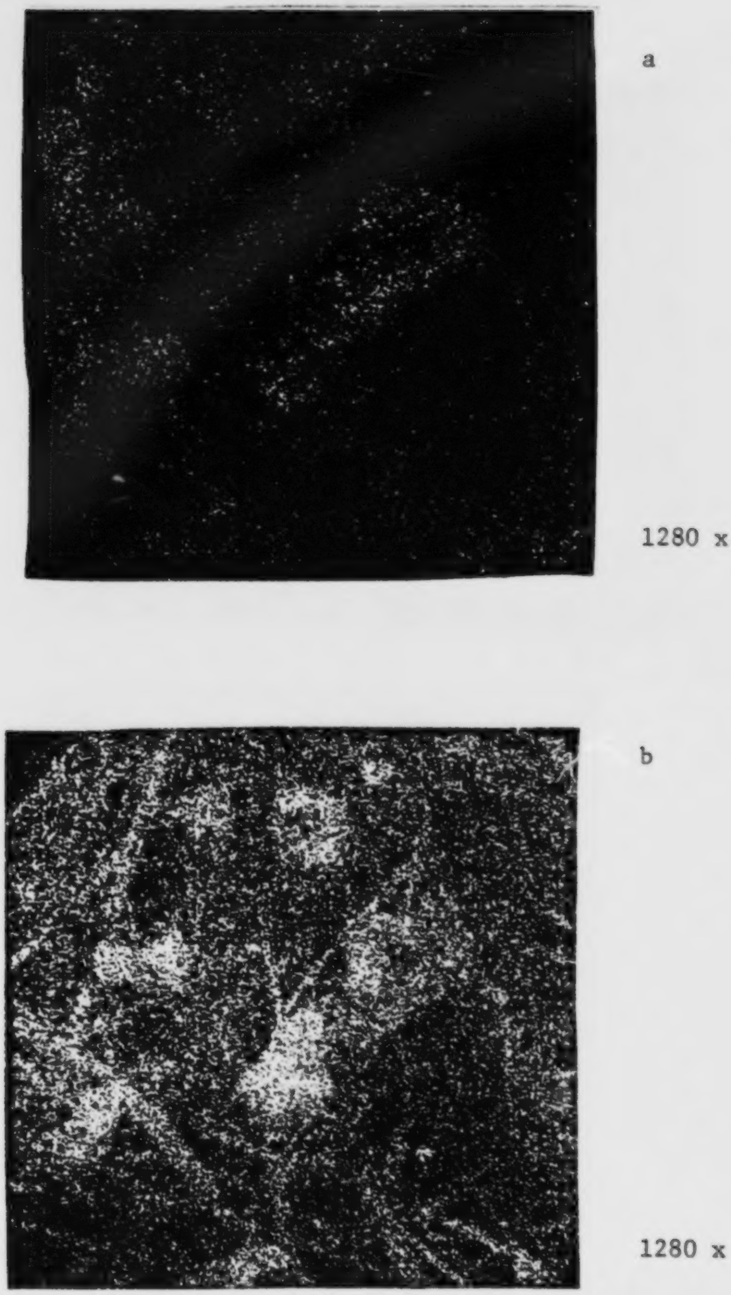

a
1280 x
b
1280 x

Figure 4.25. Electron microprobe element map of region shown in Figure 4.23.
(a) Aluminum map; (b) Silicon map.

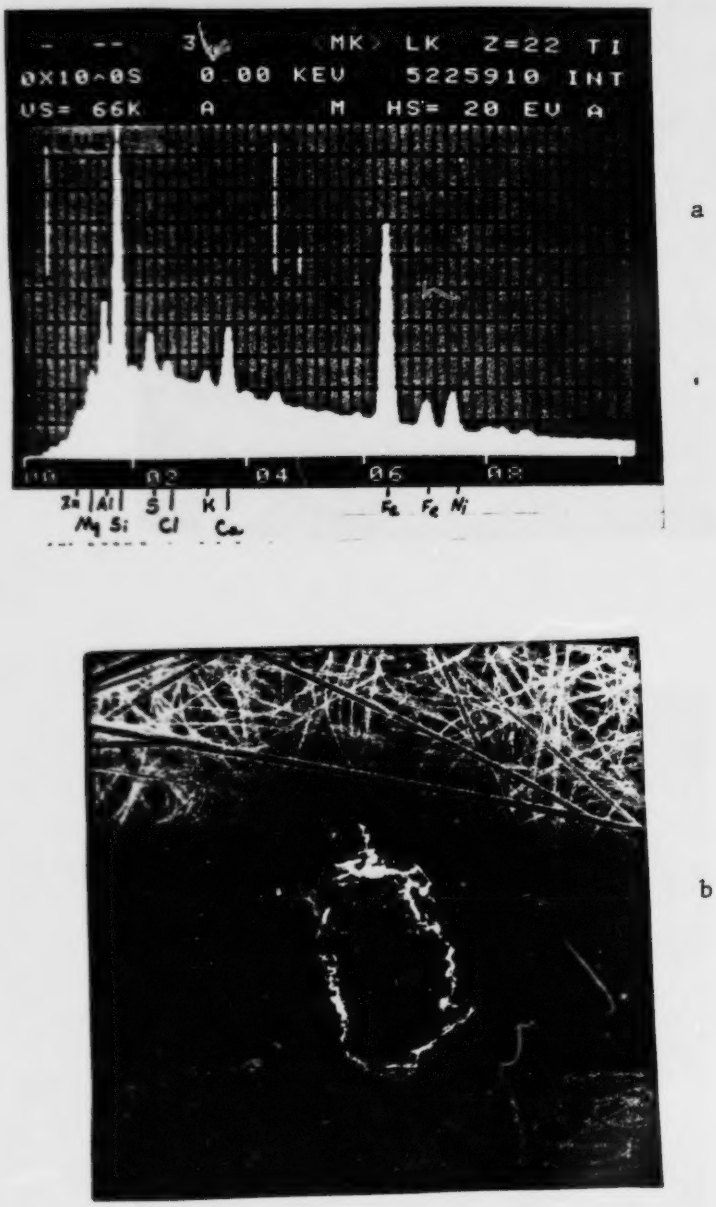
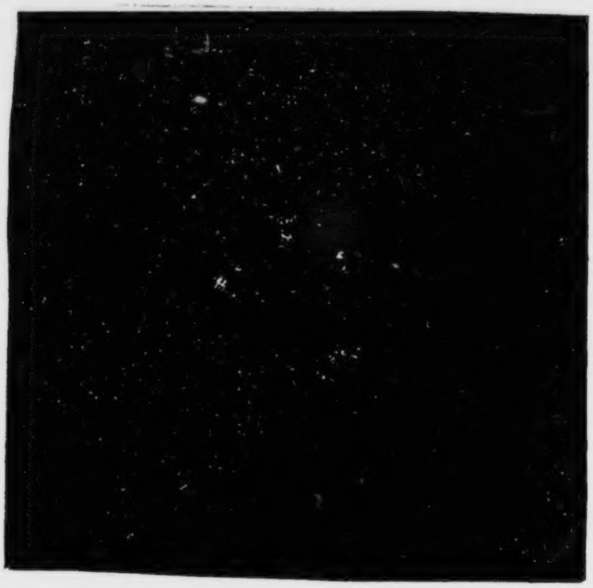


Figure 4.26. Electron microprobe spectrum (a) and scanning electron micrograph (b) of a region on an air sample collected on a glass fiber filter. Sample Volume: 0.1 m^3 air. Location: Great Lakes Chemical Corp., El Dorado, Arkansas. Collected 9/22/76


a
520 x

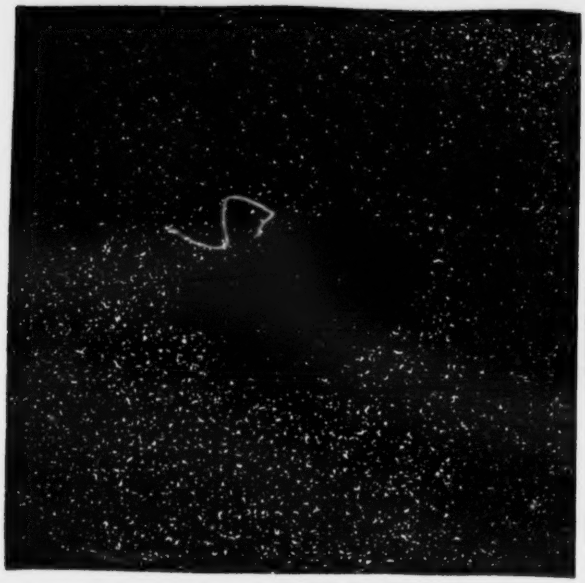
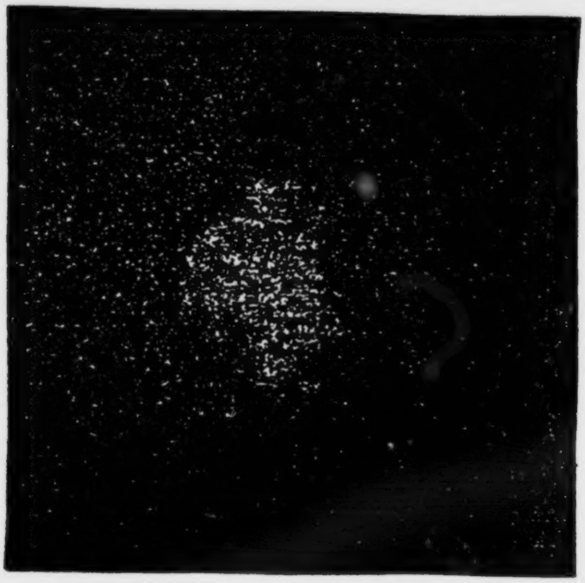

b
520 x

Figure 4.28. Electron microprobe element map of region shown in Figure 4.26.
(a) Potassium map; (b) Calcium map.



520 x

Figure 4.29. Electron microprobe element map of region shown in Figure 4.26.
Magnesium map.

Table 4.16. NEUTRON ACTIVATION ANALYSIS OF AMBIENT AIR HI-VOL SAMPLES

Site	Date	Medium	Br (μg/m^3)	Cl (μg/m^3)
GRL[a]	12/13/76-	GFF[b]	0.089	N.D.
	12/14/76	CF[c]	0.230	0.043
GRL	12/16/76-	GFF	0.574	0.345
	12/17/76	CF	0.24	0.086
GRL	12/17/76-	GFF	20.2	1.70
	12/18/76	CF	2.44	0.40

[a] All were 24 hr samples.

[b] GFF = glass fiber filter.

[c] CF = cellulose filter.

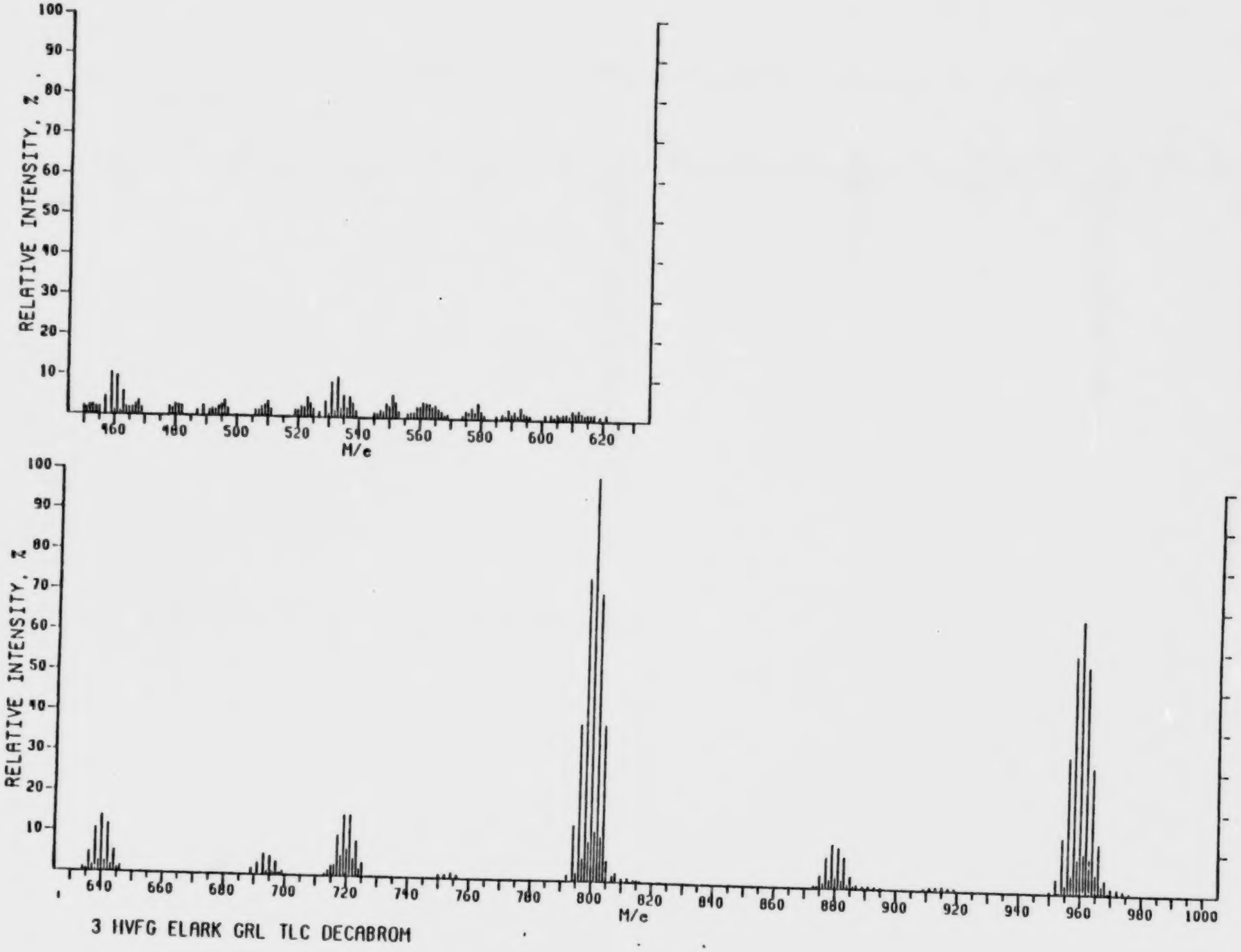


Figure 4.30. Mass spectrum of GFF-TLC Extract Obtained by Direct Probe.

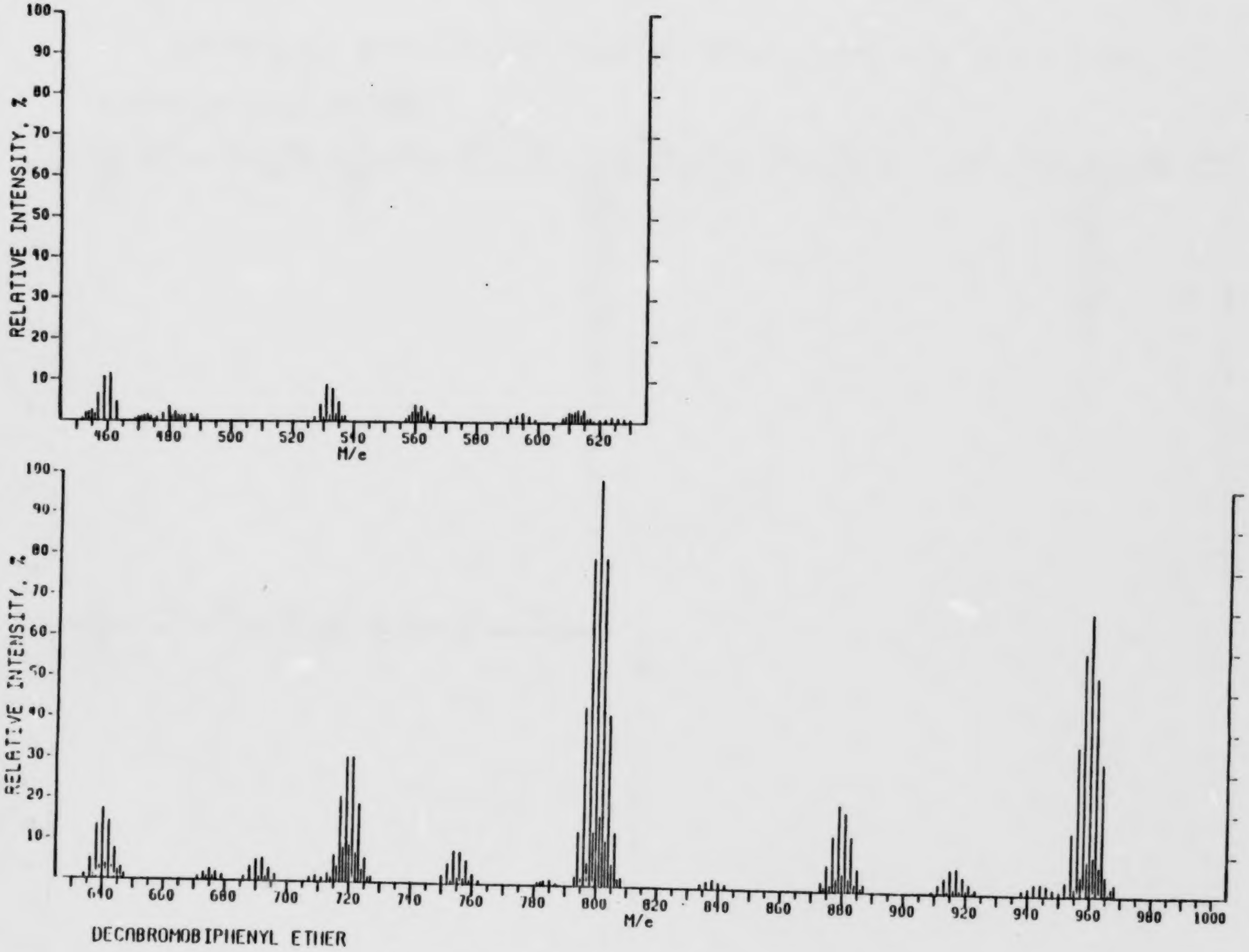


Figure 4.31. Mass spectrum of authentic Decabrom.

was eluted and subjected to GC/MS/COMP. The GC/MS spectrum is shown in Figure 4.32 along with the spectrum of authentic Tetrabrom.

Table 4.17. ANALYSIS OF HI-VOL FILTERS FOR DECABROM

Date	Filter Type	Decabrom (ng/m^3)
12/13, 14/76	GFF[a]	<13.3
	CF[b]	<16.5
12/16, 17/76	GFF	94.3
	CF	22.9
12/17, 18/76	GFF	118
	CF	113

[a] GFF = glass fiber filter

[b] CF = cellulose filter

4.2.2.3 Inorganics in Ambient Air

Chloride/Bromide and Chlorine/Bromine.--The results obtained by turbidimetric determination of total halide and halogen are given in Table 4.18. The site, period and cycle designation were given in the sampling protocols (Table 4.13) and the location on the schematic maps (Fig. 4.16-4.18).

Sampling was performed on two days yielding a total of three sets of impinger samples. During Period 1, halides were detected at L4 (Fig. 4.16) adjacent to the holding pond. During Period 2 halides were found at L2 (Fig. 4.17) downwind of the bromine extraction and ethylene dibromide facilities. At 1304 to 1309 hours an upset occurred. At 1430 hours Cycle 4 for halides and halogens was initiated (Fig. 4.18). Both halides and halogens were found in some of these samples. Neutron activation analysis indicated low, but detectable, amounts of bromide in L3 and L4 (Table 4.19); however, the NAA bromine value for L2 is inconsistent with both the orientation with respect to the meteorological conditions and of course the halide and total halogen value. Cycle 6 which was taken four hours after the upset showed the highest halide values at L3 and L4 (Fig. 4.18), but no detectable halogens. Neutron activation analysis depicted no detectable bromine or bromide at L3 which gave the highest total halide values. There

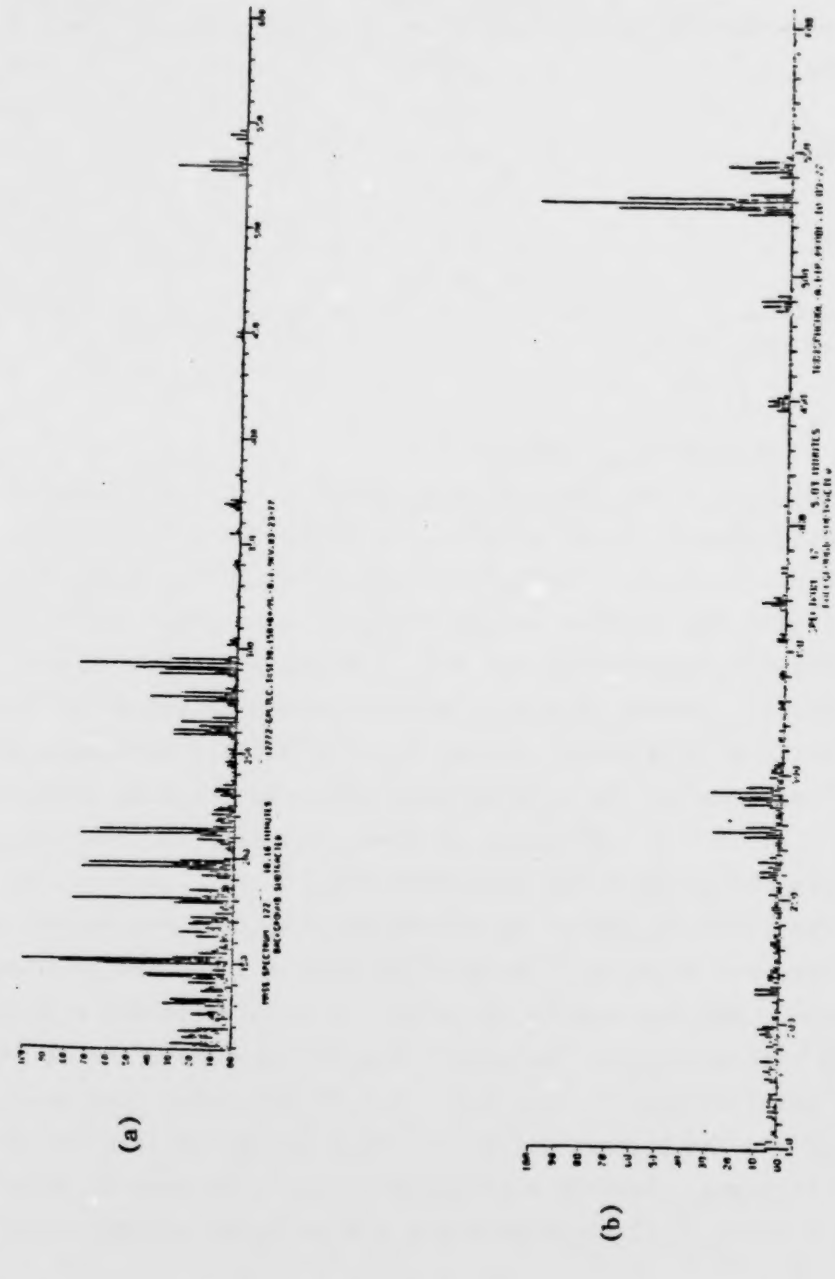


Figure 4.32. Mass spectrum of (a) GFF-TLC extract and (b) authentic Decabrom obtained by GC/MS/COMP.

Table 4.18. CONCENTRATIONS OF HALOGENS AND HALIDES IN AMBIENT AIR SURROUNDING GREAT LAKES CHEMICAL CORP.[a,b]

		Cl_2/Br_2					Cl^-/Br^-				
Period	Cycle	L1	L2	L3	L4	L7	L1	L2	L3	L4	L7
P1	C3	–[c]	–	<103	<62	–	–	–	<65	53 ± 8	–
P2	C3	<130	<65	<81	–	–	<90	140 ± 0	<56	–	–
P3	C4		<79	60 ± 12	<67	183 ± 17	–	–	186 ± 4	137 ± 37	61 ± 86
P3	C6		–	<77	<71	<94	–	–	876 ± 11	324 ± 20	<61

[a] Values in $\mu g/m^3$.

[b] Determined by turbidity.

[c] Not analyzed.

Table 4.19. CONCENTRATIONS OF BROMIDE AND BROMINE IN AMBIENT AIR SURROUNDING GREAT LAKES CHEMICAL CORP.[a,b]

		Br_2					Br^-				
Period	Cycle	L1	L2	L3	L4	L7	L1	L2	L3	L4	L7
P1	C3	–[c]	–	<42	–	–	–	–	<21	–	–
P2	C3	–	–	–	–	–	–	–	–	–	–
P3	C4	–	484	<24	<27	<16	–	<17	28	26	<47
P4	C6	–	–	<32	–	–	–	–	<16	–	–

[a] Values in μg/m^3.

[b] By Neutron Activation Analysis.

[c] Not analyzed.

is some question about this value since ion exchange chromatographs showed at least 80% of the halide at L3 was bromide. In addition, glass filters and cellulose filters used in sampling cycles before and after the P3, C4 impinger sampling cycle showed high halogen concentrations at L3. There is apparently a change in the prevalent species between Cycle 4 and 6 from halogens to halide. More detailed studies should be required to verify this change and determine its etiology.

Fluoride/Fluorine.--No fluoride or fluorine could be detected in any samples taken of ambient air surrounding Great Lakes Chemical Corp. (Table 4.20). The limits of detection were 0.012 ppm in the impinger solution based on the volume of air sampled and the sensitivity of the turbidimetric method.

Table 4.20. CONCENTRATIONS OF FLUORIDE/FLUORINE IN AMBIENT AIR SURROUNDING GREAT LAKES CHEMICAL CORP.[a,b]

		Locations				
Period	Cycle	L1	L2	L3	L4	L7
P1	C3	-	-	<4.2	<2.6	-
P2	C3	<5.4	<2.7	<3.4	-	-
P3	C4	-	<3.4	<2.4	<2.7	<3.2
P3	C6	-	-	<2.8	<2.6	<3.9

[a] Values in $\mu g/m^3$.

[b] Determined by ion specific electrode method.

Acid Mist.--No titratable acid was found in any samples. Table 4.21 summarizes the upper limit of ambient air concentration of acid mist.

Table 4.21. ACID MIST IN AMBIENT AIR SURROUNDING GREAT LAKES CHEMICAL CORP. AS H_2SO_4[a]

		Location
Period	Cycle	L3
P1	C4	<45
P2	C5	<43

[a] Values in $\mu g/m^3$.

4.2.2.4 Organic Vapors in Ambient Air

Qualitative Analysis by High Resolution GC/MS/COMP.--Figures 4.33 and 4.34 depict the total ion current and ion chromatograms of organic volatiles which were collected at L3 on the Great Lakes Corp. site (Fig. 4.18 for sampling location). Several halogenated compounds were identified. They were bromopropane, 1,2-chlorobromoethane, 1,2-dibromoethane, 1-chloro-3-bromopropane, bromoform and bromobenzene. The sampling location was on top of a three-story facility which was not in operation and is normally used

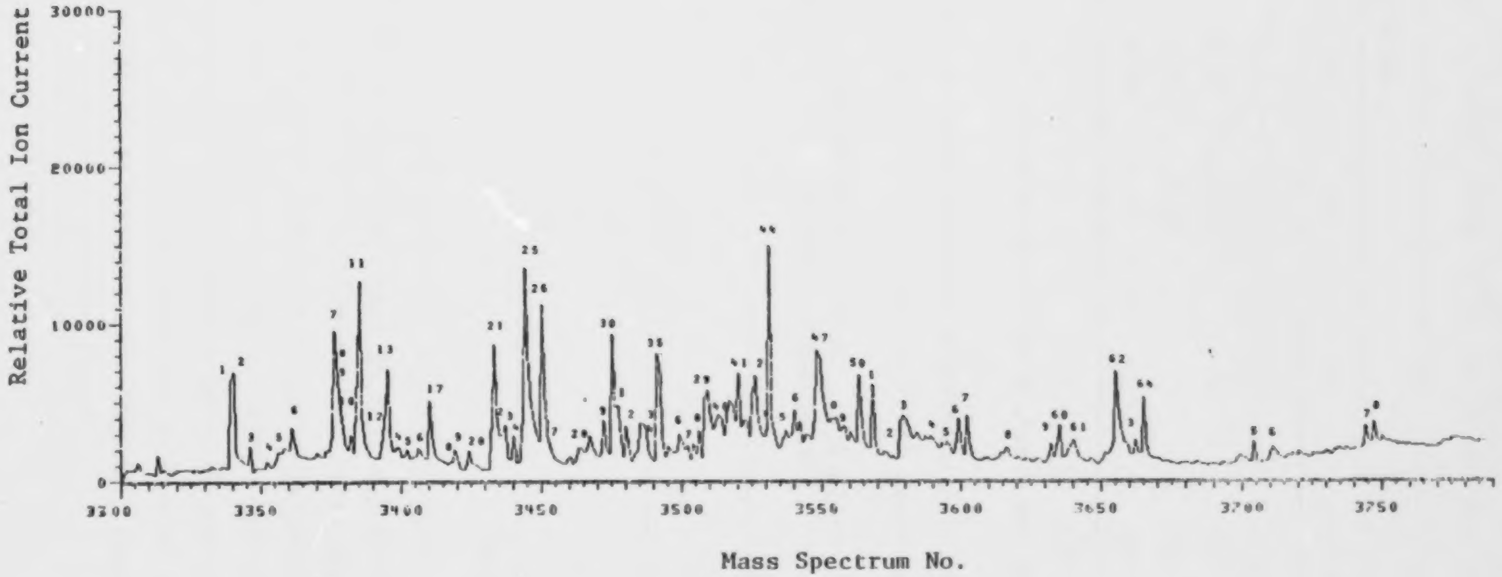


Figure 4.33. Total ion current profile of ambient air sample from Great Lakes Corp. site, El Dorado, Arkansas (P3/C1/L3).

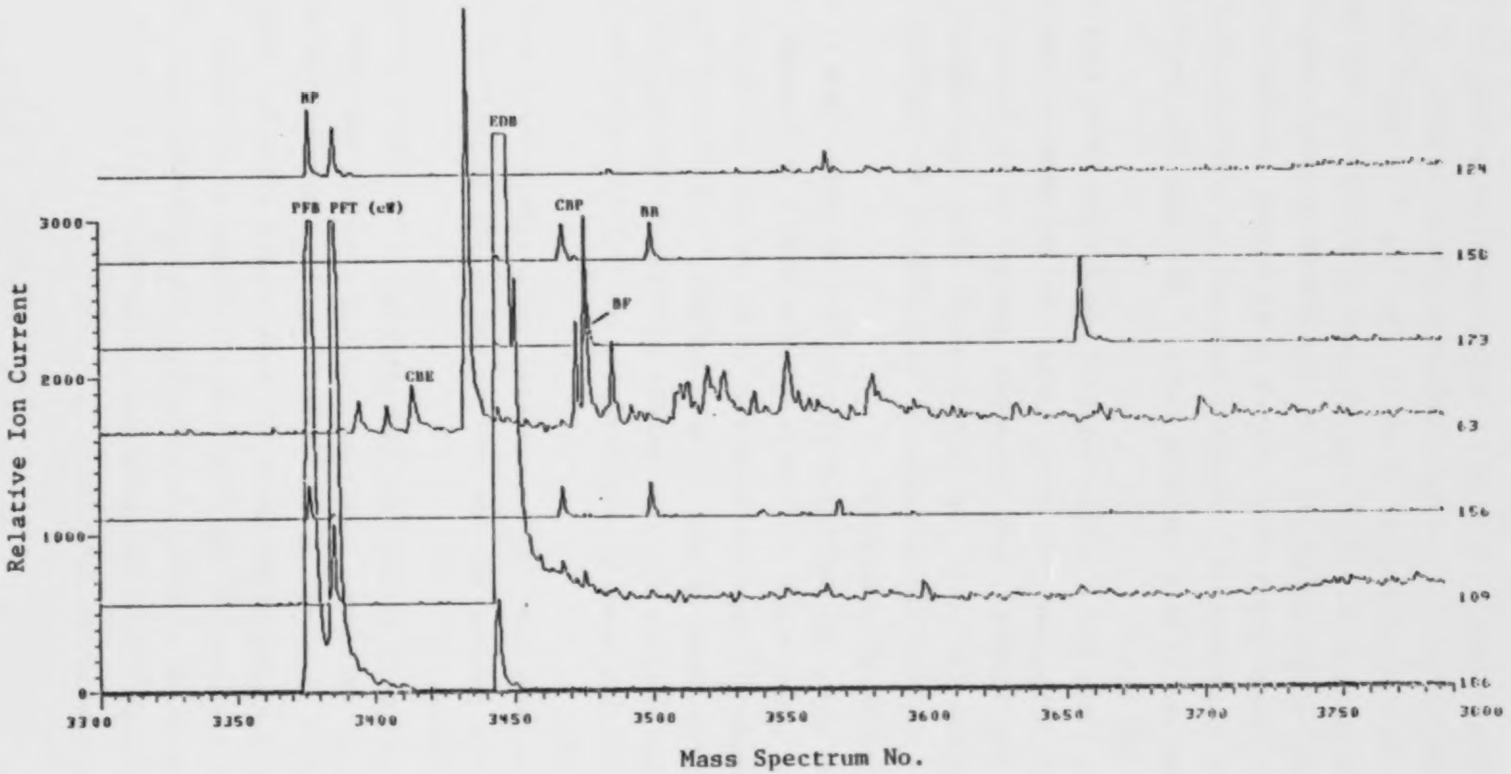


Figure 4.34. Ion chromatograms of ambient air sample from Great Lakes Corp. site, El Dorado, Arkansas (P3/C1/L3). BP = bromopropane, CBE = 1-chloro-2-bromoethane, EDB = ethylene dibromide, CBP = 1-chloro-3-bromopropane, BF = bromoform, BB = bromobenzene.

for the production of sodium bromide. Another sampling period was between 1740 to 945 hours (overnight) using a DuPont personal sampler. At L3 (ELV), EDB was clearly identified (Peak No. 34, Fig. 4.35 and 4.36). The results corresponding to L5 (ELV) are depicted in Figures 4.37-4.38.

On the night of September 24, 1976, two DuPont personal samplers were deployed on two water towers, one located in El Dorado and the second in Parker's Chapel on Highway 15. Samplers were set to sample at ~110 ml/min/cartridge during the 13 hour sampling period. The sampling period began at approximately 0500 hrs.

Table 4.22 lists the volatile organics which were identified in ambient air taken on the El Dorado city water tower. No halogenated compounds were identified in this sample. Most compounds appeared to be from auto exhaust. Figure 4.39 depicts the total ion current profile for this sample. Figure 4.40 represents the ion chromatogram for this ambient air sample. No brominated compounds were detected.

Table 4.23 lists the volatile organics in the ambient air at the Parker's Chapel water tower. Although we were unable to identify in the sample any brominated compounds from full mass spectral interpretation, we were able to detect them by mass fragmentography. Figure 4.41 depicts the total ion current profile for this sample and Figure 4.42 depicts the ion chromatograms. Allyl bromide, bromopropane and 1,2-dibromoethane were clearly detected.

Table 4.24 summarizes the halogenated hydrocarbons which were identified by GLC/MS/COMP in ambient air surrounding and in the vicinity of Great Lakes Chemical Corp.

Quantification of Halogenated Hydrocarbons.--Table 4.25 presents the concentrations of halogenated hydrocarbons surrrounding the Great Lakes Corp. site. Also presented in this table are the concentration of allyl bromide, 1- or 2-bromopropane and 1,2-dibromoethane which had been detected in the ambient air samples taken on Parker's Chapel water tower. The highest concentration observed were for 1,2-dibromoethane which reached a level of 1,837 ng/m^3 in a sample taken at Location 3 which was on the sodium bromide production facility.

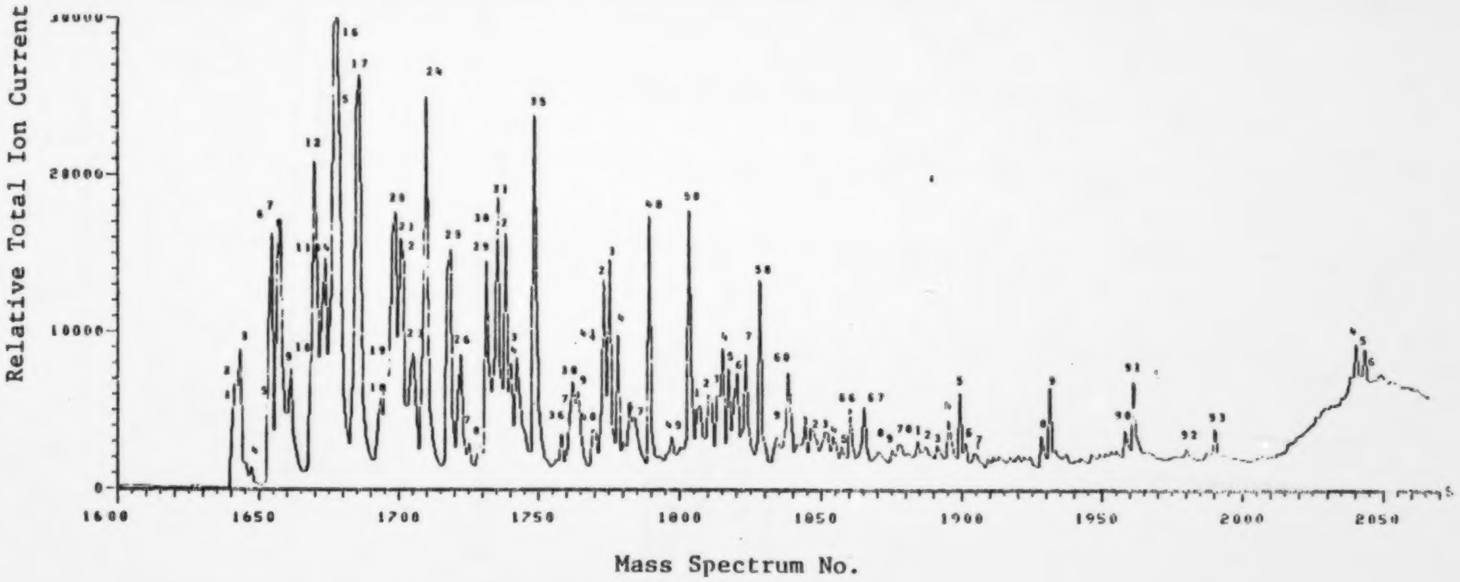


Figure 4.35. Total ion current profile of volatile ambient air pollutants from Great Lakes Corp. site, El Dorado, Arkansas (P3/C3/L3 ELV).

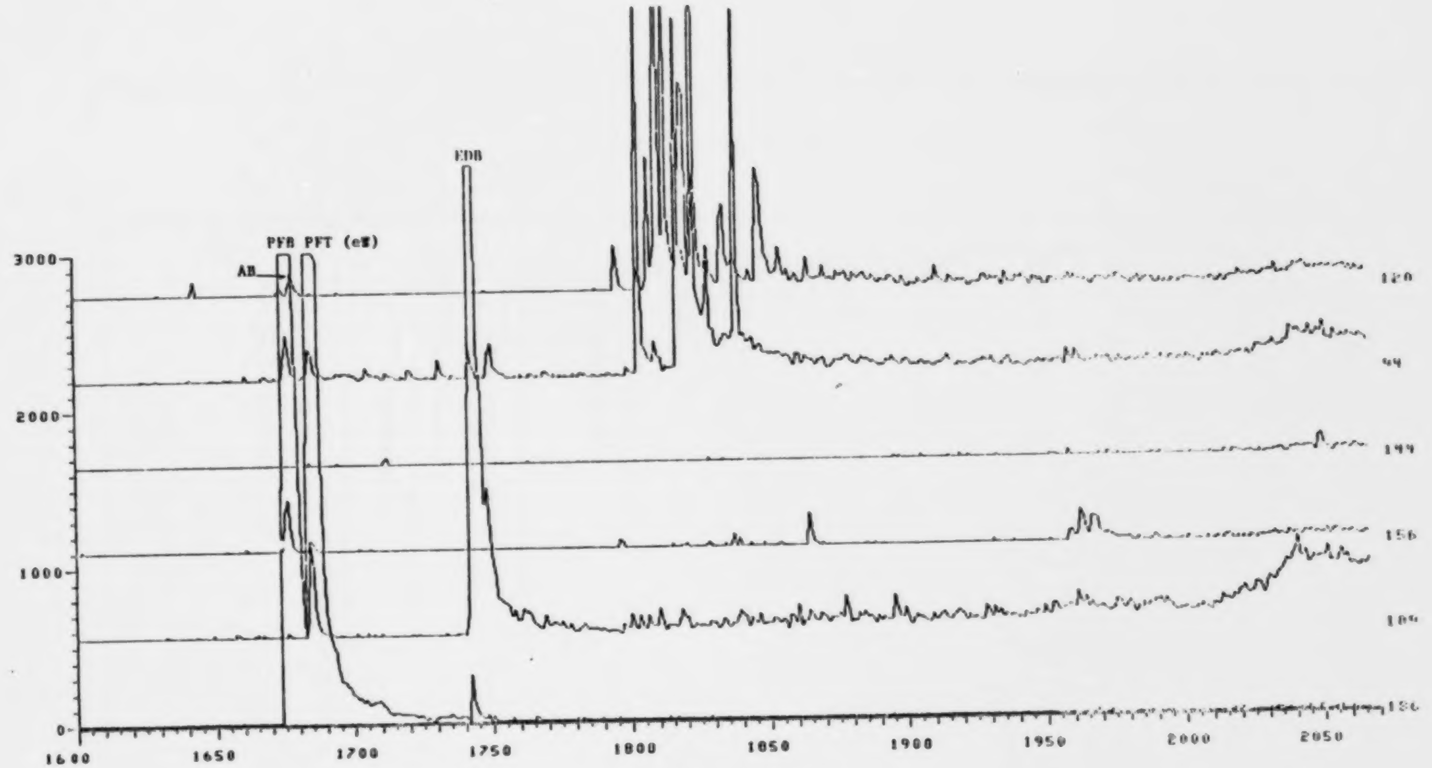


Figure 4.36. Ion chromatograms of ambient air sample from Great Lakes Corp. site, El, Dorado, Arkansas (P3/C3/L3 ELV). AB = allyl bromide, EDB = 1,2-dibromoethane.

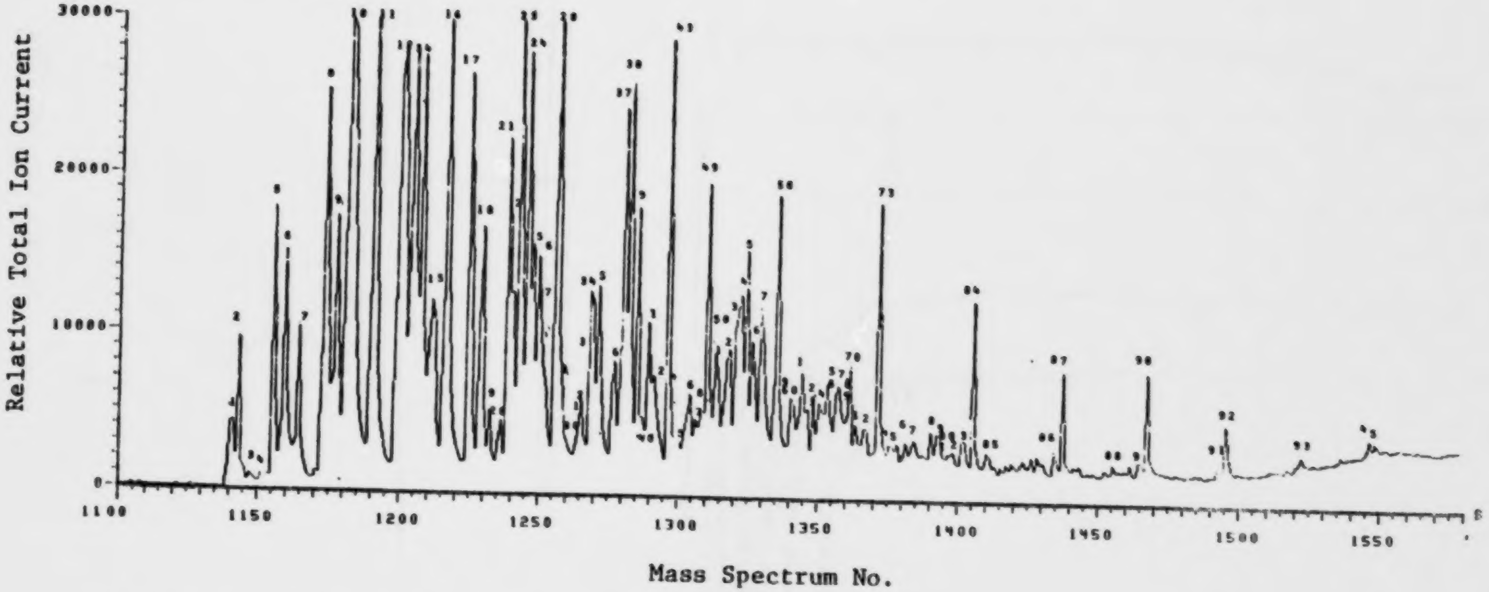


Figure 4.37. Total ion current profile of volatile ambient air pollutants from Great Lakes Corp., El Dorado, Arkansas (P3/C3/L5 ELV).

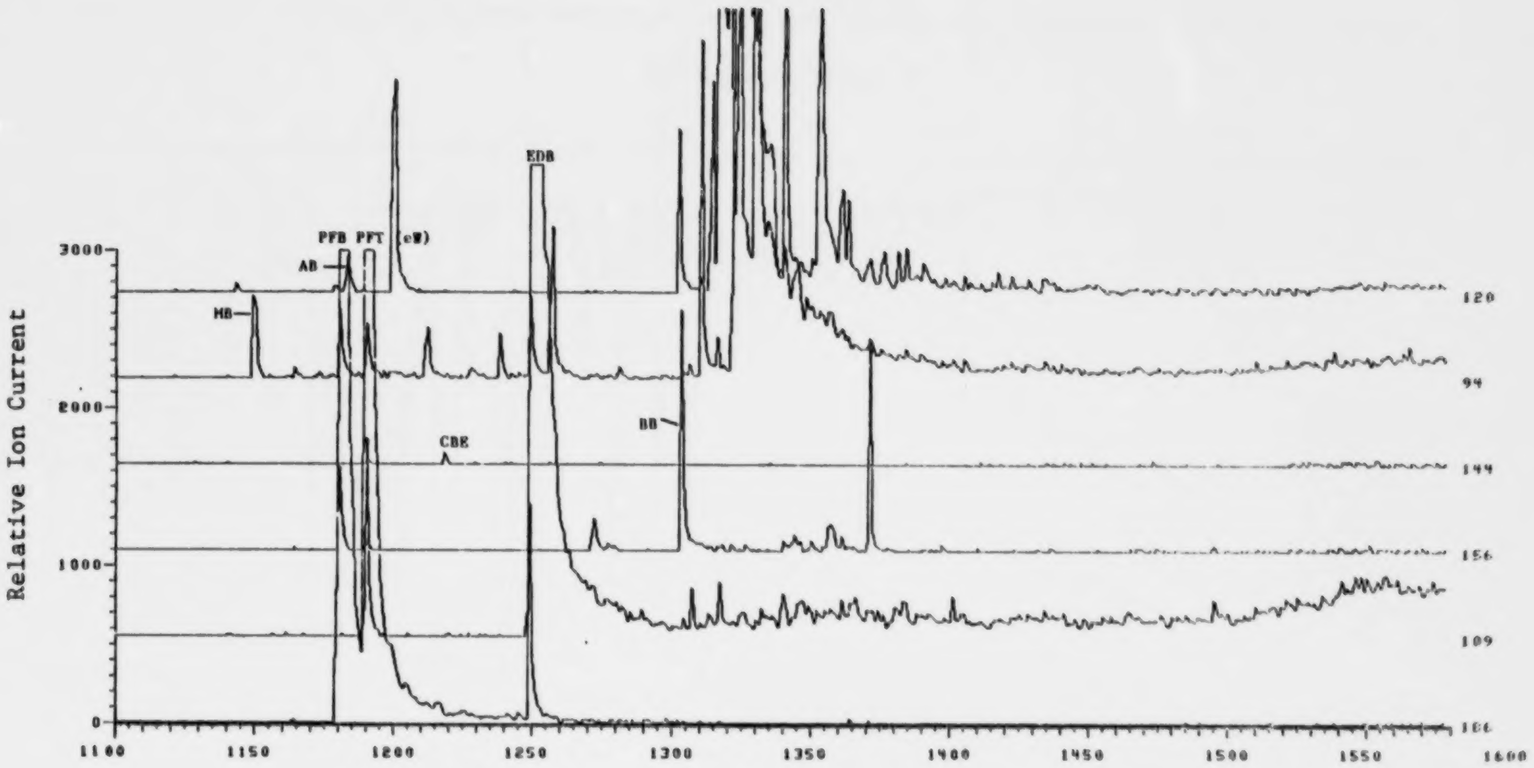


Figure 4.38. Ion chromatograms of ambient air sample from Great Lakes Corp. site, El Dorado, Arkansas (P3/C3/L5 ELV). MB = methyl bromide, AB = allyl bromide, CBE = 1-chloro-2-bromoethane, EDB = ethylene dibromide, BB = bromobenzene.

Table 4.22. VOLATILE ORGANICS IDENTIFIED IN AMBIENT AIR TAKEN ON EL DORADO, ARKANSAS CITY WATER TOWER[a]

Chromatographic Peak No.	Elution Temperature (°C)	Compound
1	44	dichlorodifluoromethane
1A	44	*n*-butane
2	46	acetaldehyde
3	47	isopentane
4	47	trichlorofluoromethane
5	48	acetone + C_5H_{10} isomer
6	50	dichloromethane + freon 113 (BKG)
6A	51	*n*-pentane
6B	52	isopropanol
7	54	2-methylpentane
7A	54	butenal isomer
8	55	3-methylpentane
8A	56	*n*-butanal
9	57	hexafluorobenzene (eS)
9A	57	*n*-hexane
9B	58	chloroform
10	61	methylcyclopentane + perfluorotoluene (eS)
10A	64	C_7H_{14} isomer
10B	65	C_7H_{16} isomer
10C	66	benzene
10D	66	carbon tetrachloride
10E	67	cyclohexane
10F	68	2-methylhexane
10G	68	2,3-dimethylpentane
10H	69	3-methylhexane
10I	71	*n*-pentanal
10J	72.	C_7H_{14} isomer
11	73	*n*-heptane
12	78	methylcyclohexane
12A	80	C_8H_{16} isomer
13	81	C_8H_{18} isomer
13A	84	C_7H_{14} isomer
13B	84	C_8H_{18} isomer
14	85	toluene
15	87	C_8H_{18} isomer
15A	89	C_8H_{18} isomer
15B	90	4-methyl-2-pentanone
16	91	*n*-hexanal + 3-methylpentanal
17	94	*n*-octane
17A	95	tetrachloroethylene
18	95	C_8H_{16} isomer
19	98	C_8H_{16} isomer
20	101	ethylcyclohexane
21	103	C_9H_{18} isomer
22	105	ethylbenzene
23	107	*p*-xylene
23A	108	C_9H_{20} isomer
23B	109	C_9H_{18} isomer
24	110	C_9H_{20} isomer
25	111	styrene + C_9H_{20} isomer
25A	111	2,3-dimethylpentanal
26	112	*n*-heptanal
26A	114	C_9H_{18} isomer
27	115	*n*-nonane
28	119	isopropylbenzene
28A	119	C_9H_{18} + $C_{10}H_{22}$ isomer
28B	122	$C_{10}H_{20}$ isomer
28C	122	$C_{10}H_{12}$ isomer
29	123	$C_{11}H_{24}$ isomer
29A	124	C_9H_{18} isomer
30	125	benzaldehyde
30A	127	$C_{10}H_{22}$ + C_3-alkyl benzene isomers
31	128	$C_{10}H_{22}$ + $C_{10}H_{20}$ isomers
31A	129	$C_{11}H_{24}$ isomer
31B	130	$C_{10}H_{22}$ isomer
32	131	octanone isomer
33	133	*n*-octanal
34	134	$C_{10}H_{20}$ isomer
35	135	*n*-decane
35A	136	$C_{10}H_{20}$ isomer
35B	137	$C_{10}H_{20}$ isomer
36	138	$C_{11}H_{24}$ isomer
37	140	$C_{11}H_{24}$ isomer
38	142	$C_{11}H_{24}$ isomer
39	143	$C_{10}H_{20}$ isomer
40	144	acetophenone
41	146	$C_{11}H_{24}$ isomer
42	148	$C_{11}H_{24}$ isomer
43	149	2-nonanone
44	151	*n*-nonanal

(continued)

Table 4.22 (cont'd)

Chromatographic Peak No.	Elution Temp. (°C)	Compound
44A	152	$C_{11}H_{22}$ isomer
45	153	*n*-undecane
46	155	C_4-alkyl benzene isomer
46A	160	phenylpropenal isomer
47	162	dimethylphenol isomer
48	167	2-decanone
49	169	*n*-decanal
50	171	*n*-dodecane
50A	172	$C_{13}H_{28}$ isomer
50B	173	$C_{12}H_{24}$ isomer
51	173	$C_{10}H_{16}$ isomer

[a] Ambient air sampled with DuPont personal sampler (*ca*. 110 ml/min) on 9/24-9/25/76 from 2000-900 hr.

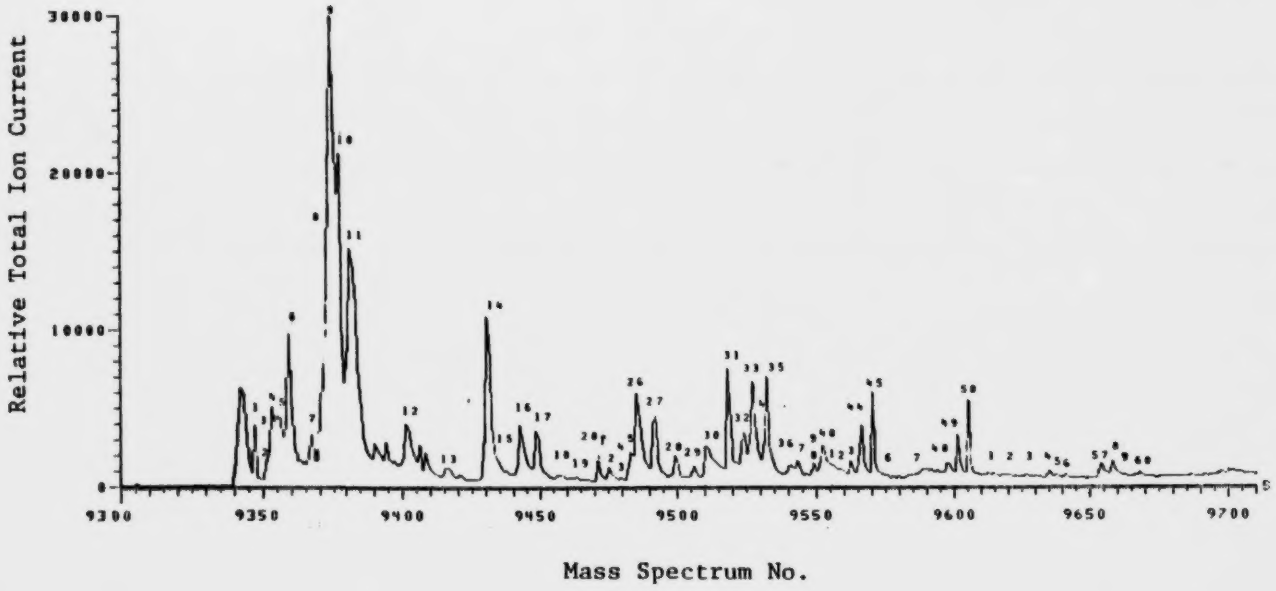


Figure 4.39. Total ion current profile of volatile ambient air pollutants taken on El Dorado, Arkansas city water tower.

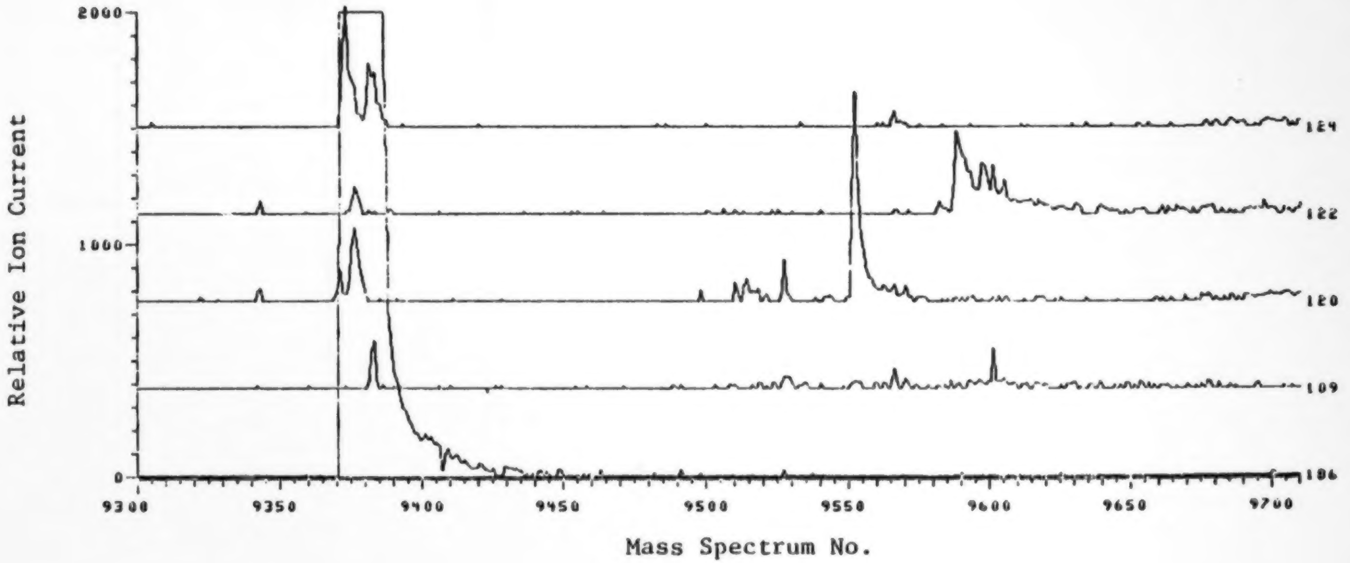


Figure 4.40. Ion chromatograms of ambient air sample from top of El Dorado city water tower in Arkansas.

Table 4.23. VOLATILE ORGANICS IDENTIFIED IN AMBIENT AIR TAKEN ON PARKER'S CHAPEL WATER TOWER NEAR EL DORADO, ARKANSAS[a]

Chromatographic Peak No.	Elution Temperature (°C)	Compound
1	45	butane + dichlorodifluoromethane
2	47	acetaldehyde
2A	47	isopentane
3	48	trichlorofluoromethane
4	49	propanal + C_5H_{10} isomer
5	49	*n*-pentane
5A	50	acetone
5B	50	C_5H_{10} isomer
6	51	dichloromethane + fluorotrichloromethane
6A	52	isopropanol
6B	54	C_6H_{12} isomer
7	55	2-methylpentane
8	57	3-methylpentane
8A	57	C_6H_{12} isomer
9	58	hexafluorobenzene (es)
10	59	*n*-hexane
10A	59	chloroform
11	62	perfluorotoluene (es)
11A	63	methylcyclopentane
12	64	1,1,1-trichloroethane
12A	65	butanal isomer
12B	66	C_7H_{14} isomer
12C	66	C_6H_{10} isomer
13	67	benzene
13A	67	carbon tetrachloride
14	68	cyclohexane
14A	69	C_7H_{14} isomer
15	69	2-methylhexane
15A	70	2,3-dimethylpentane
16	71	3-methylhexane
16A	72	methyl isopropyl ketone
17	72	dimethylcyclopentane isomer + pentanal
18	73	methylhexane isomer + trichloroethylene
19	73	C_7H_{14} isomer
20	75	*n*-heptane
20A	77	C_7H_{14} isomer
21	79	methylcyclohexane
21A	80	C_8H_{16} isomer
22	81	2,4-dimethylhexane
23	83	1,2,3-trimethylcyclopentane
23A	83	C_8H_{16} isomer
24	85	trimethylpentane isomer
24A	85	C_8H_{16} isomer
25	86	toluene
25A	87	2,3-dimethylhexane
26	88	2-methylheptane
26A	88	4-methylheptane
27	89	3-methylheptane
27A	90	1,trans-2-dimethylcyclohexane
28	91	1,cis-2-dimethylcyclohexane
29	92	C_9H_{20} isomer
29A	92	hexanal
30	93	C_8H_{16} isomer
30A	94	C_8H_{16} isomer
31	95	*n*-octane
31A	96	tetrachloroethylene
31B	96	C_8H_{16} isomer
31C	98	C_8H_{16} isomer
32	99	C_9H_{20} isomer
32A	100	silane compound (BKG)
33	101	2,4-dimethylheptane
34	102	2-methyloctane or 2,6-dimethylheptane
35	102	ethylcyclohexane
36	103	C_9H_{20} isomer
36A	104	C_9H_{18} isomer
36B	105	trimethylcyclohexane isomer
36C	106	C_9H_{20} isomer
37	107	ethylbenzene
37A	107	trimethylcyclohexane isomer
37B	108	4-methyloctane
38	109	*p*-xylene
38A	110	C_9H_{20} isomer
39	110	*m*-xylene
40	111	3-methyloctane

(continued)

Table 4.23 (cont'd)

Chromatographic Peak No.	Elution Temperature (°C)	Compound
40A	112	styrene + C_9H_{18} isomer
40B	112	dimethylpentanal (tent.) isomer
41	113	*o*-xylene
41A	114	*n*-heptanal
42	115	methyl ethylcyclohexane isomer
42A	116	C_9H_{18} isomer
43	117	*n*-nonane
44	118	C_9H_{18} isomer
44A	119	$C_{10}H_{20}$ isomer
45	120	isopropylbenzene
45A	120	dimethyloctane isomer
46	121	tetramethylhexane isomer
47	122	$C_{10}H_{22}$ isomer
47A	123	$C_{10}H_{20}$ isomer
48	123	propylcyclohexane
49	124	$C_{10}H_{22}$ isomer
49A	125	$C_{10}H_{20}$ isomer
50	125	*n*-propylbenzene + benzaldehyde + $C_{10}H_{22}$ isomer
50A	126	$C_{10}H_{20}$ isomer
51	127	*p*-ethyltoluene
51A	127	$C_{10}H_{22}$ isomer
52	128	*m*-ethyltoluene
52A	129	$C_{10}H_{22}$ isomer
53	129	$C_{11}H_{24}$ isomer
54	130	$C_{11}H_{24}$ isomer
55	131	3-methylnonane
56	133	dimethyloctane isomer
56A	133	$C_{11}H_{24}$ isomer
57	134	*o*-ethyltoluene
57A	135	$C_{10}H_{20}$ isomer
57B	136	$C_{11}H_{22}$ isomer
58	137	*n*-decane
58A	138	C_4-alkyl benzene isomer
59	138	$C_{11}H_{24}$ isomer
59A	139	$C_{11}H_{22}$ isomer
59B	139	1,2,3-trimethylbenzene
60	140	$C_{11}H_{24}$ + C_4-alkyl benzene isomers
60A	140	$C_{12}H_{26}$ isomer
61	141	$C_{11}H_{24}$ isomer
62	142	$C_{12}H_{26}$ isomer
63	143	butylcyclohexane
63A	144	$C_{12}H_{26}$ isomer
64	145	C_4-alkyl benzene isomer
64A	145	$C_{12}H_{26}$ isomer
64B	146	*n*-butylbenzene + propyltoluene isomer
64C	146	$C_{11}H_{22}$ isomer
65	147	$C_{12}H_{26}$ isomer
66	148	$C_{11}H_{24}$ isomer
67	149	$C_{12}H_{26}$ isomer
68	149	$C_{12}H_{26}$ isomer
69	150	$C_{11}H_{22}$ isomer
70	151	$C_{11}H_{24}$ isomer
70A	151	$C_{12}H_{24}$ isomer
71	152	$C_{11}H_{22}$ isomer
71A	153	$C_{11}H_{24}$ isomer
72	153	nonanal
72A	154	$C_{11}H_{22}$ isomer
73	155	*n*-undecane
73A	157	$C_{12}H_{24}$ isomer
73B	163	$C_{12}H_{26}$ isomer
73C	165	$C_{13}H_{28}$ isomer
73D	170	$C_{12}H_{26}$ isomer
73E	173	*n*-dodecane (tent.)
73F	191	$C_{15}H_{32}$ isomer

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[a] Ambient air sampled with DuPont personal sampler (*ca*. 110 ml/min) on 9/24-9/25/76 from 2130-930 hr.

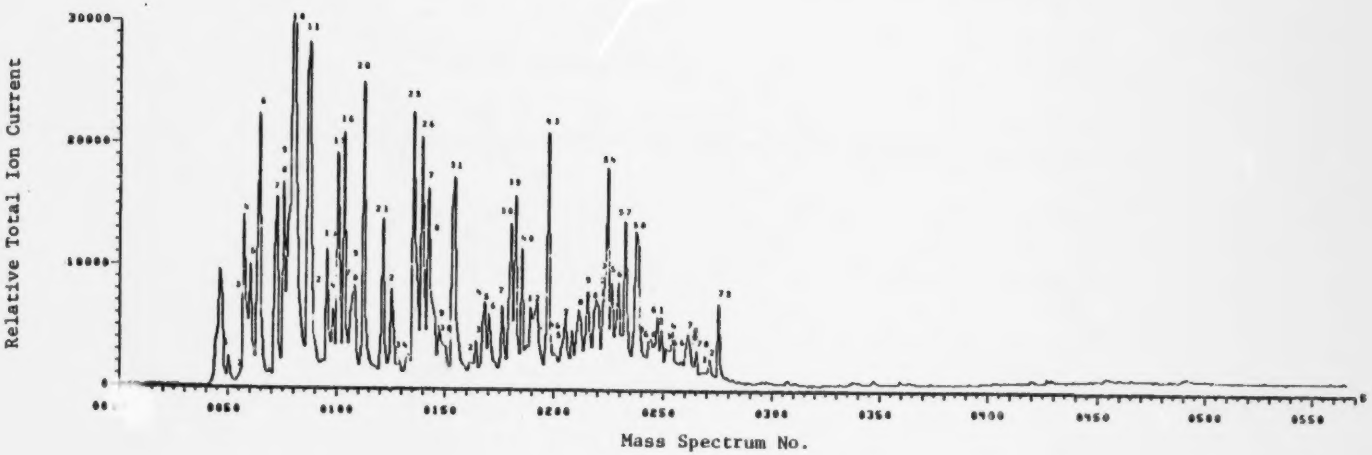


Figure 4.41. Total ion current profile of volatile ambient air pollutants taken on Parker's Chapel water tower near El Dorado, Arkansas.

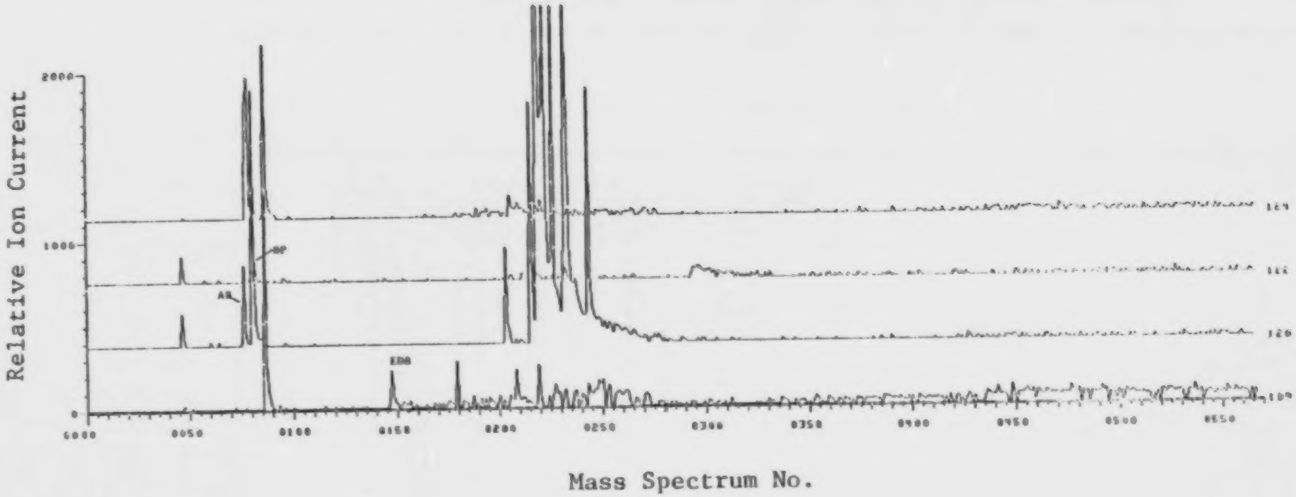


Figure 4.42. Ion chromatograms of ambient air sample from top of Parker's Chapel water tower near El Dorado, Arkansas. AB = allyl bromide, BP = bromopropane, and EDB = 1,2-dibromoethane.

Table 4.24. HALOGENATED HYDROCARBONS IDENTIFIED BY GC/MS/COMP IN AMBIENT AIR AT GREAT LAKES CORP., EL DORADO, ARKANSAS

Compound
Bromobenzene
Bromoethane
Bromofluoromethane (tent.)
Bromoform
1-Chloro-2-bromoethane
1-Chloro-3-bromopropane
1,2-Dibromoethane
1,3-Dichloropropane
Methyl Bromide
Methyl Chloride
Pentachloroethane (tent.)
Vinyl Bromide

Table 4.25. HALOGENATED HYDROCARBONS IDENTIFIED AND QUANTITATED IN AMBIENT AIR SURROUNDING GREAT LAKES CORP., EL DORADO, AK

Period/Cycle/Location[a]	Allyl bromide	Bromobenzene	Bromodichloromethane	Bromoform	1 or 2-Bromopropane	1-Chloro-2-bromoethane	1-Chloro-3-bromopropane	1-Chloro-2,3-dibromopropane	1,2-Ethylene dibromide	Methyl bromide	Vinyl bromide
P3/C1/L1	–[b]	–	1.9	–	13.4	–	–	–	7.4	–	–
L2	8.4	20.7	9.6	15.1	10.8	2.8	–	–	1,107	–	–
L3	–	60	15	11.96	16.8	6.6	23.7	–	1,837	–	–
L4	–	–	–	–	15.4	–	–	T[c]	–	–	–
P3/C3/L4	T	–	T(?)	–	55	–	–	–	–	?	–
L6 (ELV)	8	–	26.4	–	16	13	–	–	430	–	–
P3/C3/L3 (ELV)	–	–	–	–	4	–	T	–	89	–	–
L5 (ELV)	2.5	25	–	–	11.8	0.3	T	–	500	?	?
E.D., AK water tower	–	–	–	–	–	–	–	–	–	–	–
P.C., AK water tower	24.8	–	–	–	25.2	–	–	–	7.2	–	–

[a] Refer to Table 4.13 for sampling protocol, values are in ng/m^3.
[b] – = not detected
[c] T = trace detected

Estimation of Methyl Chloride, Methyl Bromide, Vinyl Chloride and Vinyl Bromide.--None of these substances occurred at levels which were quantifiable by GC/ECD or mass fragmentography. The LOD for methyl chloride and methyl bromide was 200 and 120 μg/m^3, respectively, by GC/ECD. For mass fragmentography the LOD was about 20 ppb.

Ethylene.--The levels of ethylene detected represented typical background levels as observed for all samples (Table 4.26).

Table 4.26. ETHYLENE LEVELS IN AMBIENT AIR

Site	Period/Cycle/Location	ppm
GRL	P1/C4/L5	1.20 ± 0.10
	P1/C4/L6	0.90 ± 0.10
	P1/C4/L7	0.90 ± 0

4.2.2.5 Brominated Organics in Water, Sediment and Soil

The samples were screened by the VOA method for the presence of EDB and other volatile brominated organics and selected samples were analyzed for semi-volatile brominated organics. The results are summarized in Table 4.27. Confirming spectra for EDB and Tetrabrom are shown in Figures 4.43 and 4.44, respectively.

4.2.3 Michigan Chemical Corporation (Velsicol)

4.2.3.1 Sampling

The sampling protocol and sample descriptions for Michigan Chemical Corp. are given in Table 4.28. The corresponding figure 4.45 designates the sampling locations for September 21, 1976. Table 4.29 and Figure 4.46 present the protocol for April 7, 1977.

4.2.3.2 Survey of Chemicals on Glass Fiber and Cellulose Filters

Scanning Electron Microscopy (SEM) and Electron Microprobe (EM) Analysis.--Samples consisting of three sampling periods, each 24 hours in length were collected at the Michigan Chemical Corp. plant site. Glass fiber filters (GFF) and cellulose filters (CF) were used in parallel sampling. Both types of filter material were examined. Sufficient sample was concentrated on the surface of the GFF to permit direct analysis without the usual carbon coating to prevent charge buildup on the sample.

Table 4.27. RESULTS OF ANALYSIS OF SOIL, SEDIMENT AND WATER SAMPLES FOR BROMINATED ORGANICS--SURVEY SAMPLING NEAR GREAT LAKES CHEMICAL CORPORATION, EL DORADO, AK

Period/Cycle/Location	Sample Type	Ethylene dibromide (μg/kg)	Decabromo-biphenyl ether (μg/kg)	Tetrabromo-bisphenol A (μg/kg)	Polybrominated biphenyls
P1/C1/L1 (4/7/77)	S/HHC	ND	16,000[a,b]	>>225,000[a,b,c]	* (tent.)[b]
	W/HHC	22[c,d]	ND[c]	ND[c]	--
L2	S/HHC	*[c]	--	--	--
	W/HHC	620[c,d]	ND[c]	ND[c]	--
L3	S/HHC	*[c]	--	--	--
P2/C1/L1 (4/22/77)	SD/HHC	ND	19,000[a,b,c]	22,000[a,b,c]	ND[b,c]
L2	W/HHC[e]	*[c]	--	--	--
L3	SD/HHC	ND	--	--	--
	W/HHC	ND	--	--	--
L4	W/HHC	ND	--	--	--

[a] Quantitated by gas chromatography-mass spectrometry with multiple ion detection (GC-MS-MID).

[b] Identity confirmed by direct probe-mass spectrometry.

[c] Confirmed by gas chromatography-mass spectrometry in the full scan mode.

[d] Quantitation by gas chromatography-electron capture detection.

[e] Scum on water.

Key:
* = Identified but not quantitated
ND = not detected
S = soil
W = water
SD = sediment
HHC = for halogenated hydrocarbon analysis

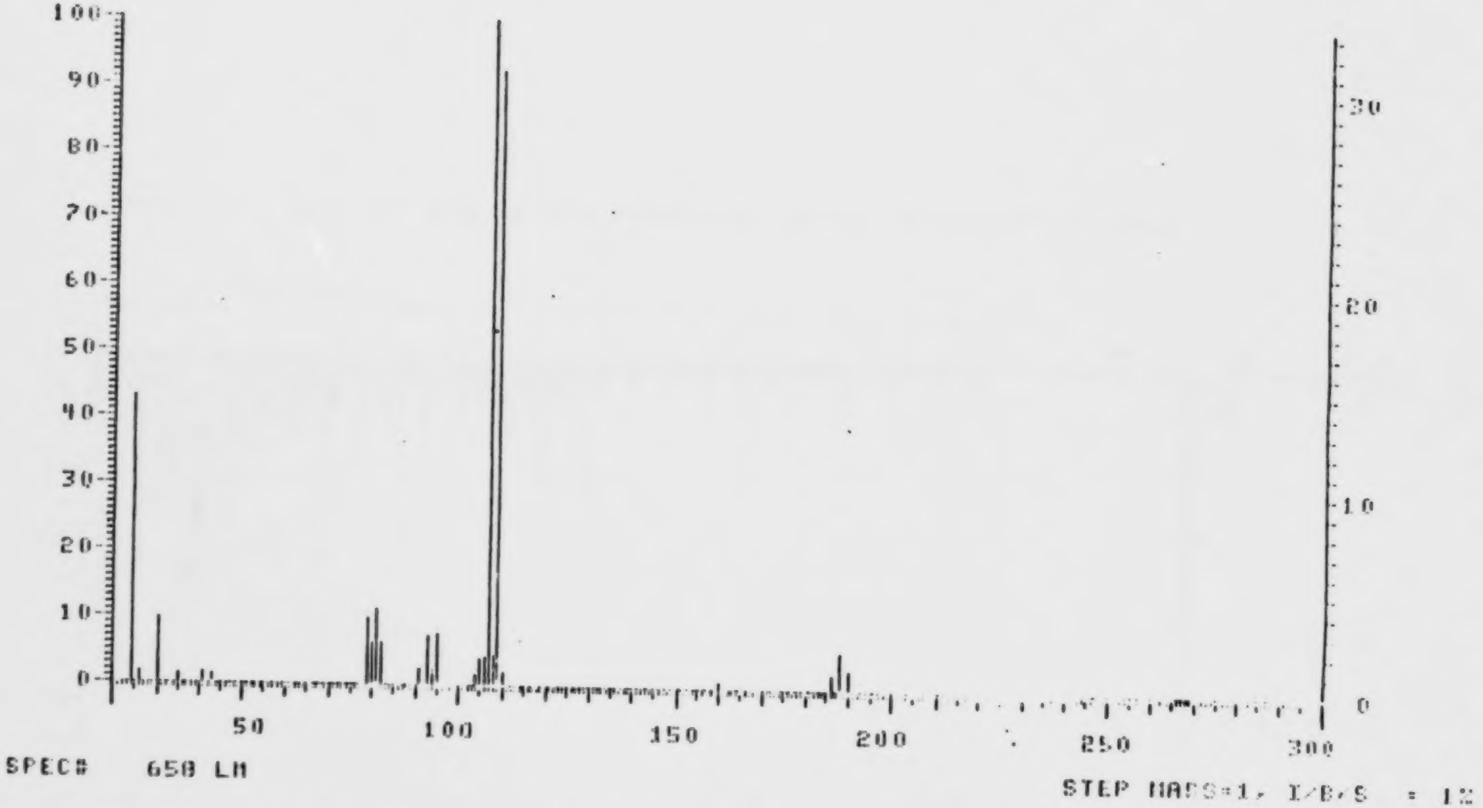


Figure 4.43. Gas chromatography/mass spectrometric analysis of volatiles purged from water collected near Great Lakes Chemical Corp., El Dorado, Arkansas (P1/C1/L2) - mass spectrum of ethylene dibromide.

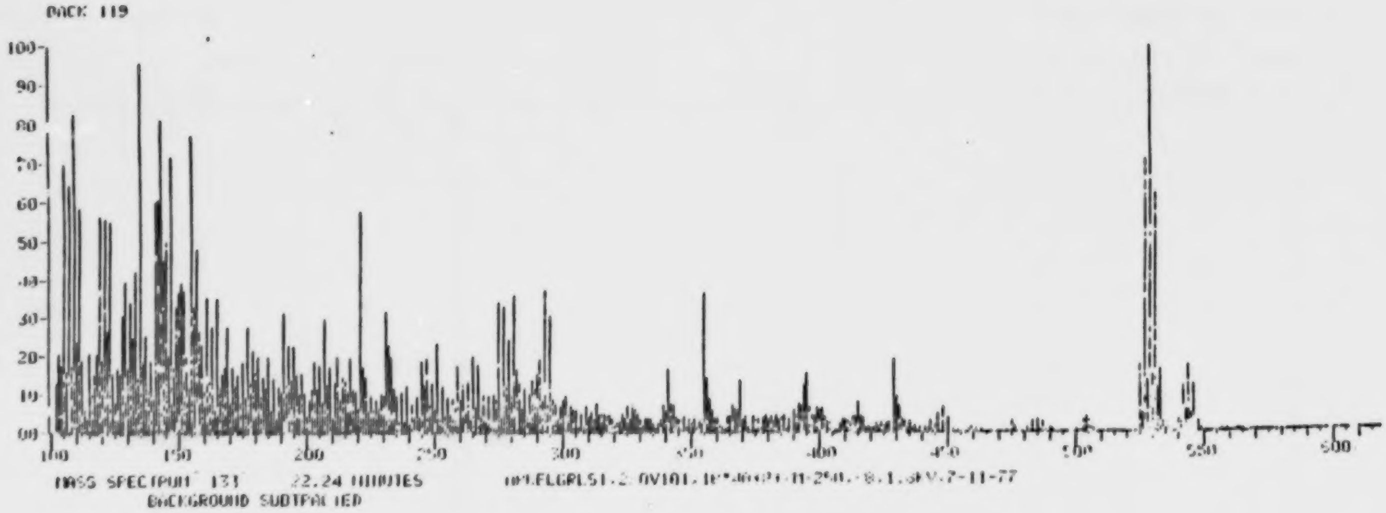


Figure 4.44. Mass spectrum of soil extract (P1/C1/L1) exhibiting Tetrabrom.

Table 4.28. SAMPLING PROTOCOL FOR MICHIGAN CHEMICAL CORPORATION, HIGHWAY 167, EL DORADO, ARKANSAS

Period	Cycle	Location	Sampling Time	Sampling Volume (ℓ)	Type of Sample	Meteorological Conditions T (°C)	% RH	Wind Dir./ Speed (kmph)	Other
9/21/76	C1	L1	1140-1415	130	HHC[a]				
		L2	1140-1411	123	HHC[a]	27-30	56	350°/8-010°/8	Clear, slightly cloudy[d]
		L3	1140-1415	171	HHC[a]	31			Clear, odor of $H_2S + Br_2$[d]
		L4	1140-1415	175	HHC[a]				[d]
	C2	L2	1140-1614	-	HHC[b]	29		358/8	Clear[d]
		L3	1140-1614	-	HHC[b]	31			[d]
		L4	1124-1625	-	HHC[b]				[d]
		L4 (ELV)	1120-1625	-	HHC[c]				
		L5 (ELV)	1105-1742	-	HHC[c]				
	C3	L1	1419-1513	48	F, CBN, CBD				
		L2	1415-1513	30	F, CBN, CBD				Br_2 plume visible
		L3	1415-1513	59	F, CBN, CBD				
		L4	1415-1513	58	F, CBN, CBD				Clear, odor of Br_2
	C4	L1	1516-1614	93	AM				
		L2	1513-1614	107	AM				
		L3	1516-1614	93	AM	31			Clear, odor of Br_2
		L4	1516-1614	91	AM				
		L3	1335	0.28	VAC				
		L4	1330	0.28	VAC				
		L5	1340	0.28	VAC				
		L1	1335	1	TED				
		L2	1330	1	TED				
		L3	1330	1	TED				
		L4	1343	1	TED				

(continued)

Table 4.28 (cont'd)

Period	Cycle	Location	Sampling Time	Sampling Volume (ℓ)	Type of Sample	Meteorological Conditions			
						T (°C)	% RH	Wind Dir./ Speed (kmph)	Other
9/21/76	C4	L1	1540	0.28	VAC			North West/11	
		L2	1548	0.28	VAC				
		L5	1548	1	TED				
		L6	1600	1	TED				

---

[a] Nutech Model 220 sampler 3-6 ft elevation

[b] DuPont sampler 3-6 ft elevation

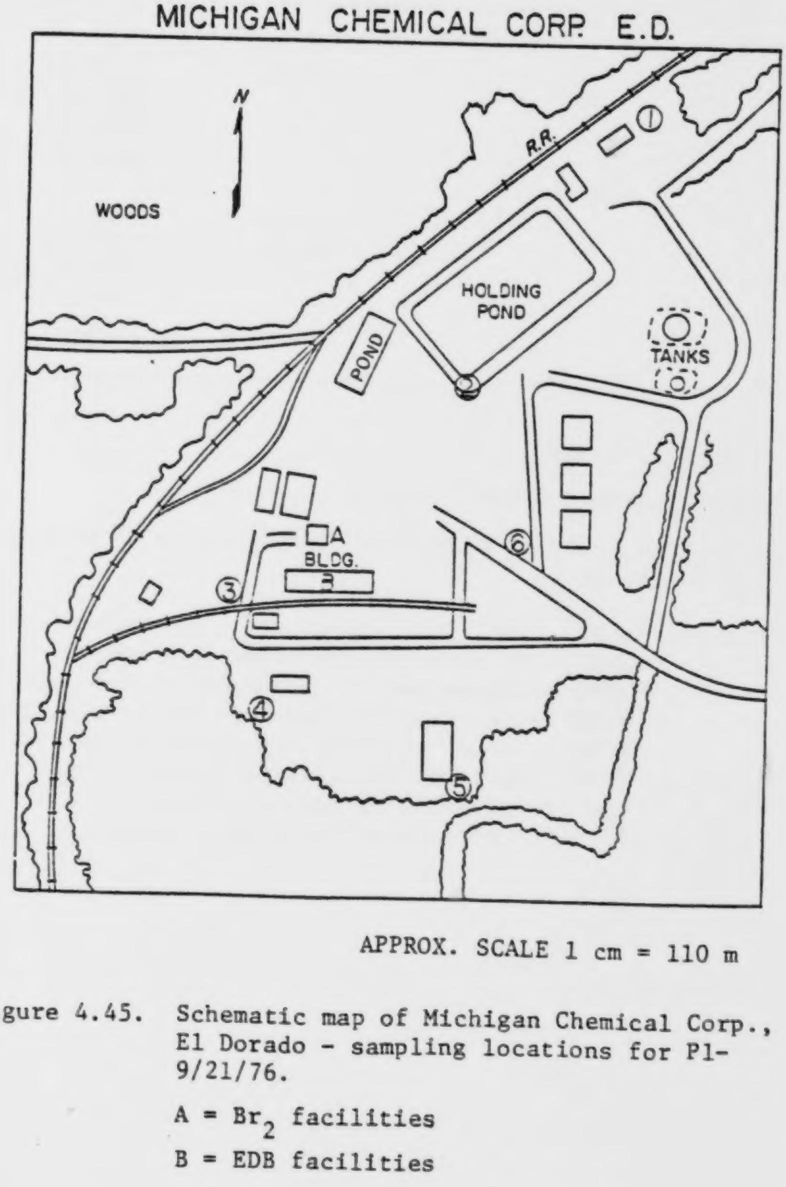
[c] DuPont sampler 15-18 ft elevation

[d] Br_2 emission visible at 1408

Locations shown in Figure 37.

Key to Sample Type:

HHC - Halogenated Hydrocarbon
F - Fluoride and Fluorine
CBN - Bromine and Chlorine
CBD - Bromide and Chloride
AM - Acid Mist
TED - Tedlar Bag
VAC - Aluminum Vacuum Can


MICHIGAN CHEMICAL CORP. E.D.
N
WOODS
R.R.
①
HOLDING POND
POND
②
TANKS
A
BLDG.
B
③
⑥
④
⑤

APPROX. SCALE 1 cm = 110 m

Figure 4.45. Schematic map of Michigan Chemical Corp., El Dorado - sampling locations for P1-9/21/76.

A = Br_2 facilities

B = EDB facilities

Table 4.29. SAMPLING PROTOCOL FOR MICHIGAN CHEMICAL CORPORATION, EL DORADO, ARKANSAS

Period	Cycle	Location	Sample Size	Type of Sample
P1 4/7/77	C1	L1	2 cores[a]	SHHC-V
			2 cores	SHHC-SV
			1 ℓ	WHHC-V/SV[b]
			--[c]	VHHC-V
				VHHC-SV
		L2	2 cores	SHHC-V
			2 cores	SHHC-SV
			1 ℓ	WHHC-V/SV[b]
			--[c]	VHHC-V
				VHHC-SV

[a] Core ∿ 5 cm diameter, 13 cm.

[b] Water was collected from standing puddles.

[c] Needles stripped from 40 cm of pine bough sampled ∿5 m above ground from trees showing damage.

Key to sample type:
SHHC - soil for halogenated hydrocarbons
WHHC - water for halogenated hydrocarbons
VHHC - vegetation for halogenated hydrocarbons
SEHHC - sediment for halogenated hydrocarbons
SCHHC - scum on water for halogenated hydrocarbons
MHHC - milk for halogenated hydrocarbons
V - for volatile organic analysis
SV - for semi-volatile organic analysis

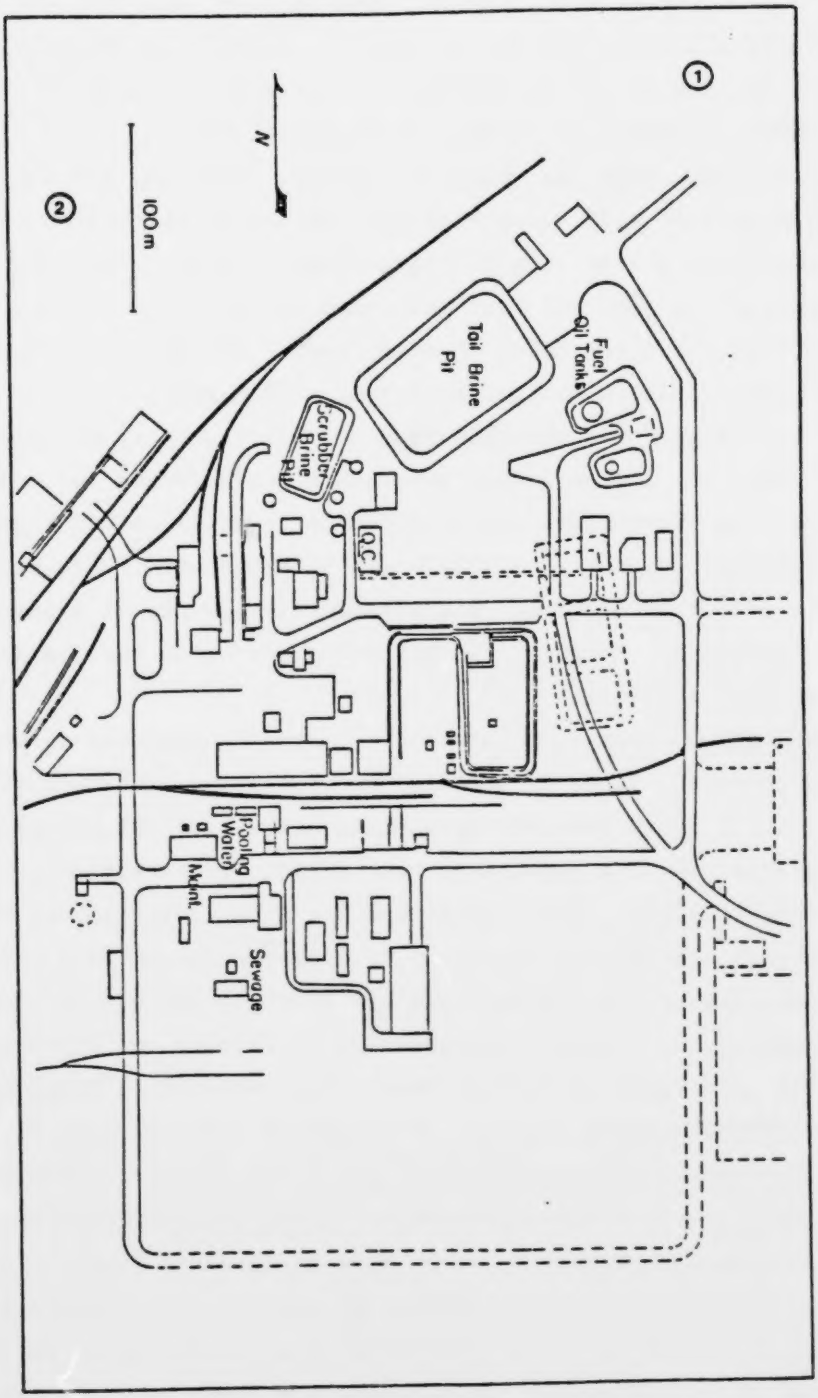

①
②
100m
N
Fuel Oil Tanks
Tail Brine Pit
Scrubber Brine Pit
Q.C.
Pooling Water
Maint.
Sewage

Figure 4.46. Schematic map of Michigan Chemical Corp. - sampling locations for 4/7/77.

Initially a search for the presence of bromine and its potential for mapping was made. In Figure 4.47, the EM spectrum from this site was expanded for greatest sensitivity in the bromine region. Traces were detectable when compared to the background in Figure 4.47. These traces were not sufficient, however, to produce an elemental map.

Electron microprobe maps for chlorine, sulfur, aluminum, and silicon are shown in Figures 4.49-4.52 along with the SEM map of the region (Fig. 4.48) for the cellulose filter from Michigan Chemical Corp. The spectrum (Fig. 4.48) depicted a higher chlorine peak than sulfur peak, the reverse of what was observed for Great Lakes Chemical Corp. In addition, aluminum, silicon and calcium are above background levels. This region was micrographed (Fig. 4.53) and mapped for chlorine, sodium, sulfur, calcium, silicon and aluminum. There was a significant substantial coincidence for sodium and chlorine, calcium and sulfur, but very little for silicon and aluminum (Fig. 4.54). Another region of the sample was carbon coated, and in this region there was almost no chlorine, but substantial amounts of calcium and sulfur appeared together. Many silicon particles appeared, but the majority are unassociated with aluminum.

Neutron Activation Analysis.--Samples of airborne particulates which had been collected by the State of Arkansas Air Pollution Control Division using a Hi-Vol sampler were examined by neutron activation for the presence of halogens, halides, etc. A segment of each filter was submitted to neutron activation analysis. The segment was 2 x 3 cm, cut from the median fold with the distal edge of the segment 3 cm from the filter edge. The results of the neutron activation analysis are shown in Table 4.30. On the third day of sampling the highest concentration of bromine and chlorine were observed for both types of filters used. The analysis of these samples for the presence of brominated organics is discussed under Section 4.2.3.5.

Gas-Liquid Chromatography/Electron Capture.--The Hi-Vol filters which were used in sampling at the Michigan Chemical Corp. site were analyzed for *tris*-(2,3-dibromopropyl)phosphate. Two by five cm segments from the central portion of the filters were cut out. Filter segments were placed in silanized 3 dram vials and extracted with 5 ml of acetone for two hours on a reciprocal shaker at approximately 120 cycles/min. These extracts were

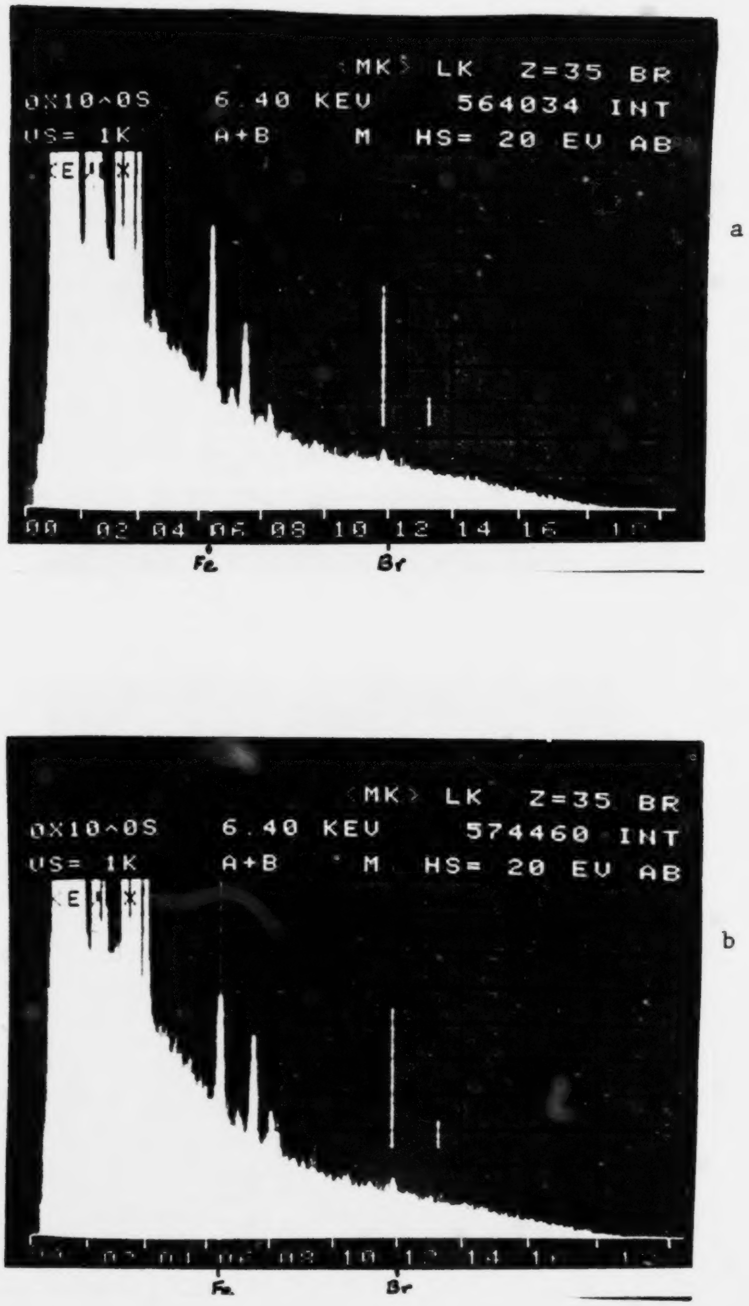


Figure 4.47. Electron microprobe spectrum of a 24 hr Hi-Vol glass fiber filter air sample taken at (a) Michigan Chemical Corporation, El Dorado, Arkansas on 12/22/76 - 12/23/76. Volume sampled 2603.6 m^3 air; (b) Great Lakes Chemical Corporation, El Dorado, Arkansas on 12/17/76 - 12/18/76. Volume sampled 2,733.6 m^3 air.

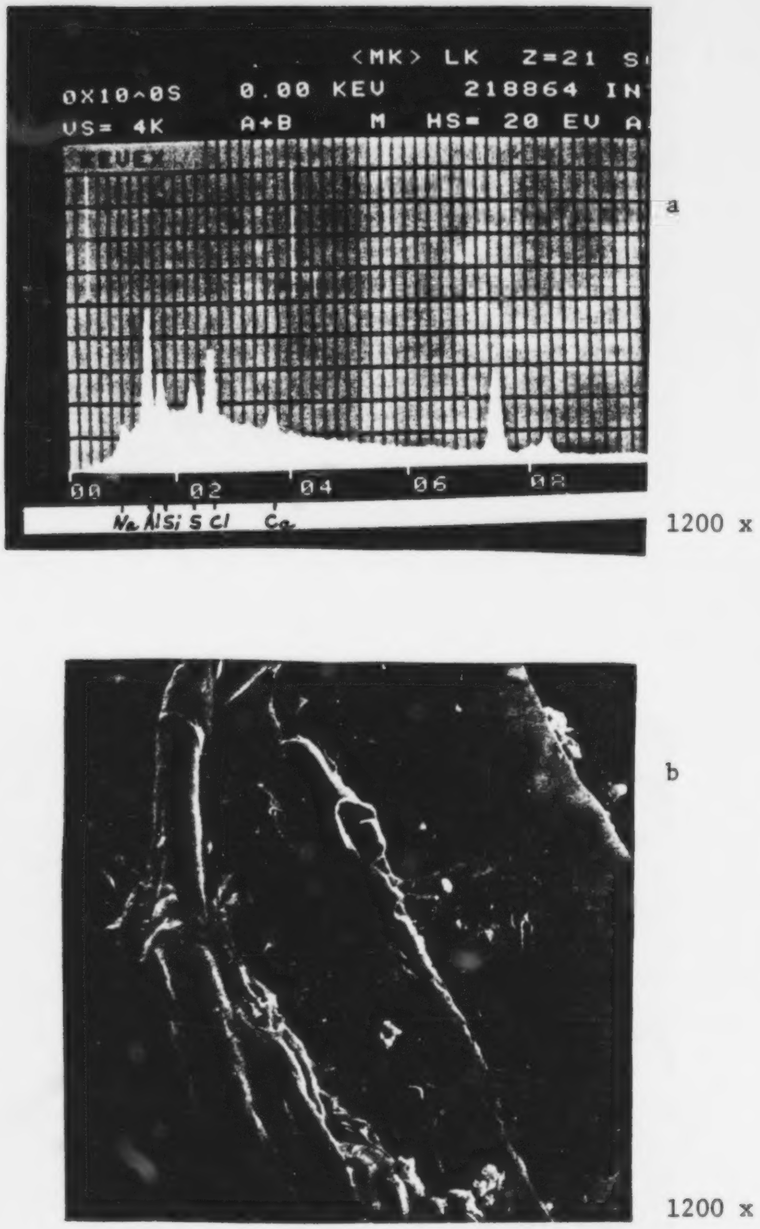


Figure 4.48. Electron microprobe spectrum (a) and scanning electron micrograph (b) of a region on an air sample collected on a cellulose filter. Sample Volume: 1463.9 m^3 air. Location - Michigan Chemical Corp., El Dorado, Arkansas. Collected 12/22/76 - 12/23/76.

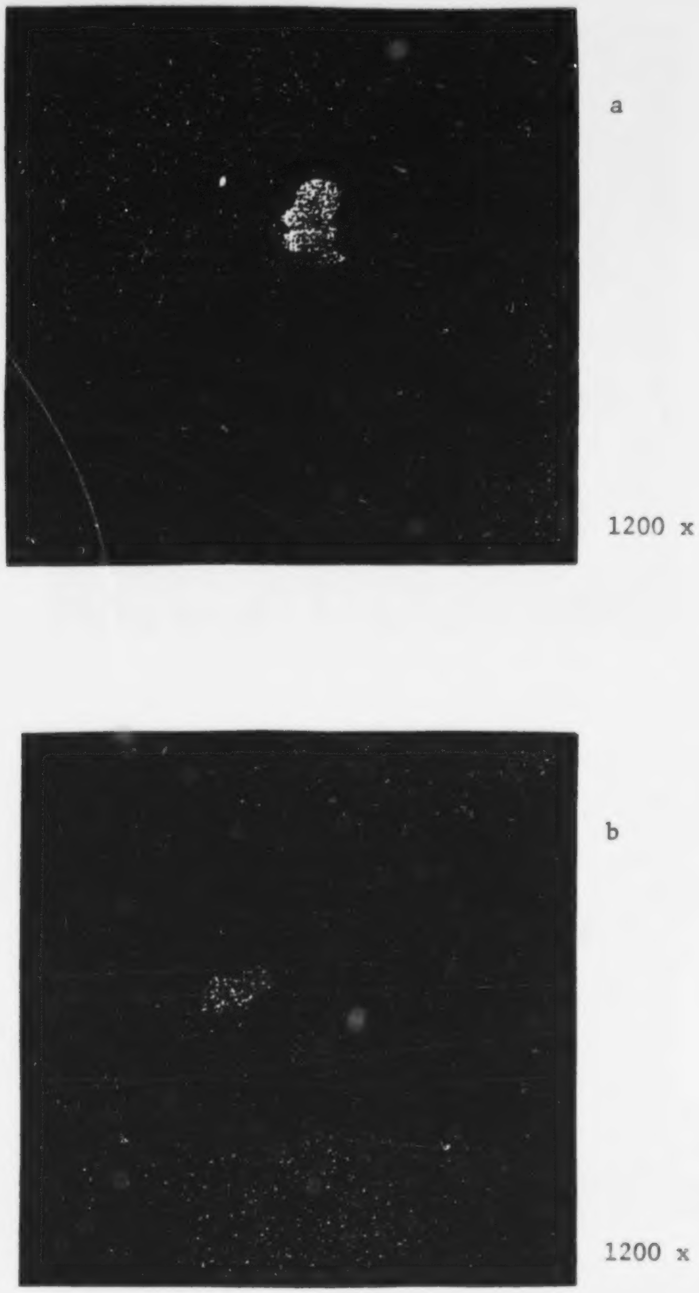

a
1200 x
b
1200 x

Figure 4.49. Electron microprobe element map of region shown in Figure 4.48.
(a) Chlorine map; (b) Sodium map.

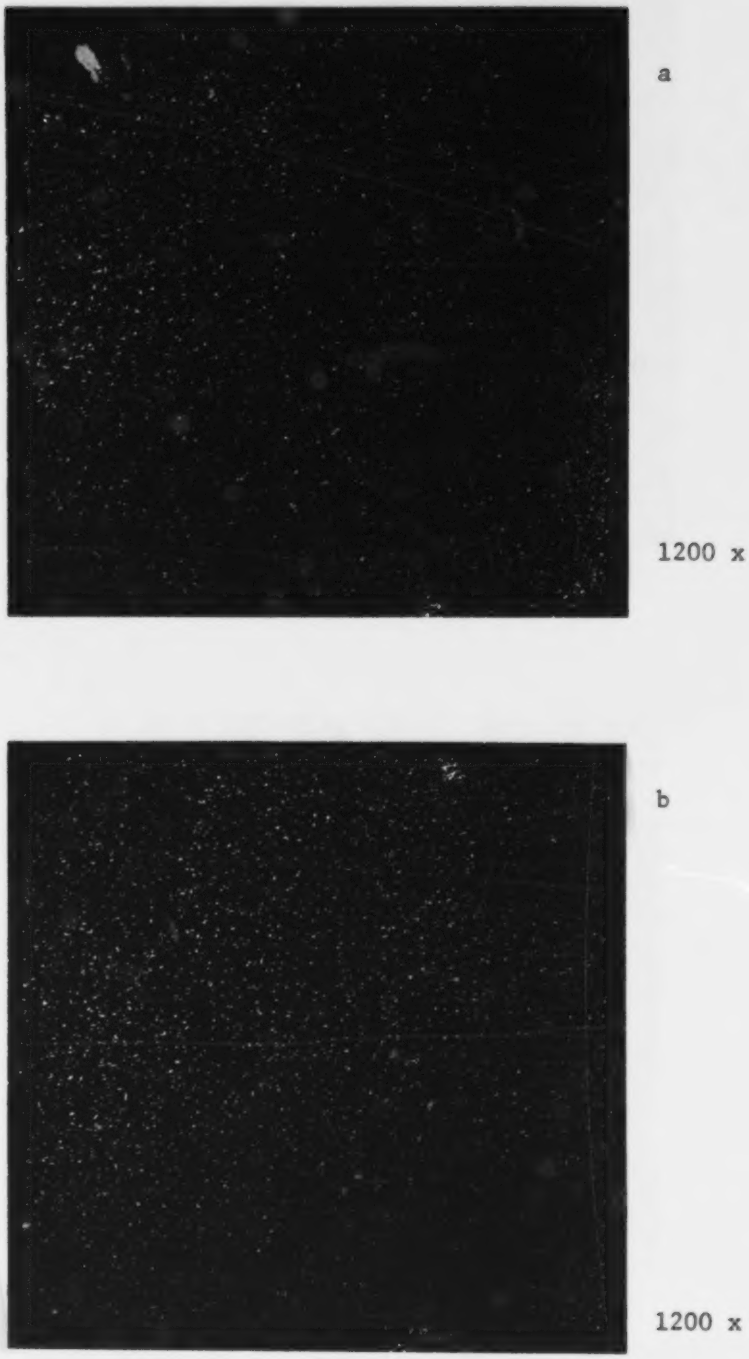

a
1200 x
b
1200 x

Figure 4.50. Electron microprobe element map of region shown in Figure 4.48.
(a) Sulfur map; (b) Calcium map.

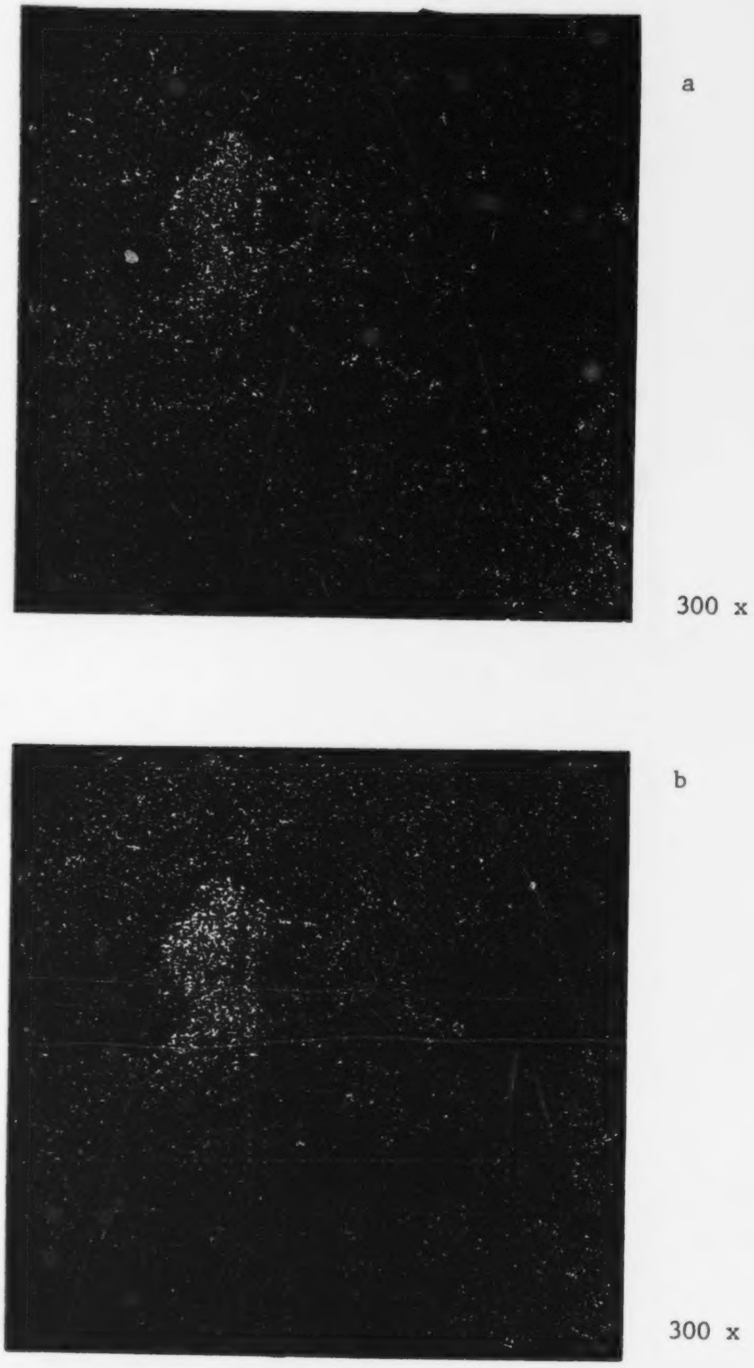

a
300 x
b
300 x

Figure 4.51. Electron microprobe element map of region shown in Figure 4.48.
(a) Calcium map; (b) Sulfur map.

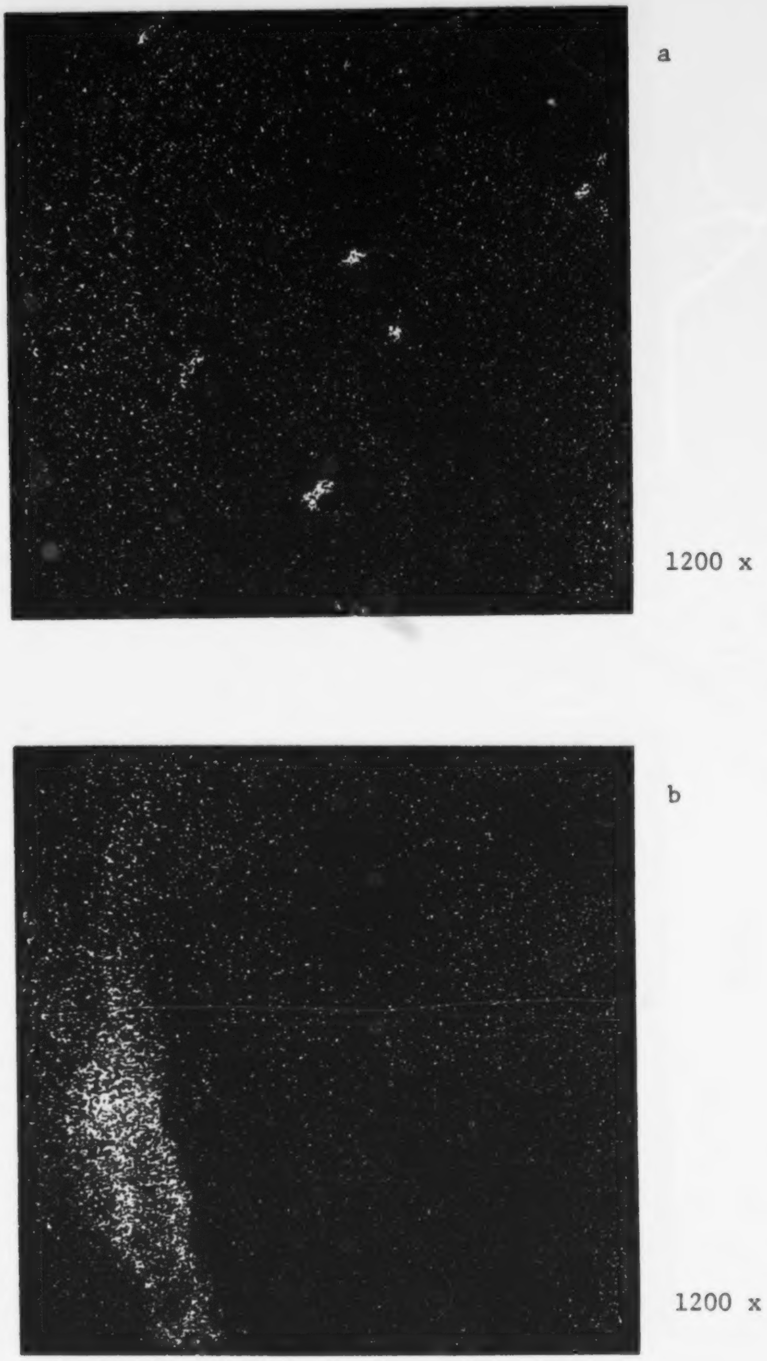

a
1200 x
b
1200 x

Figure 4.52. Electron microprobe element map of region shown in Figure 4.48.
(a) Silicon map; (b) Aluminum map.

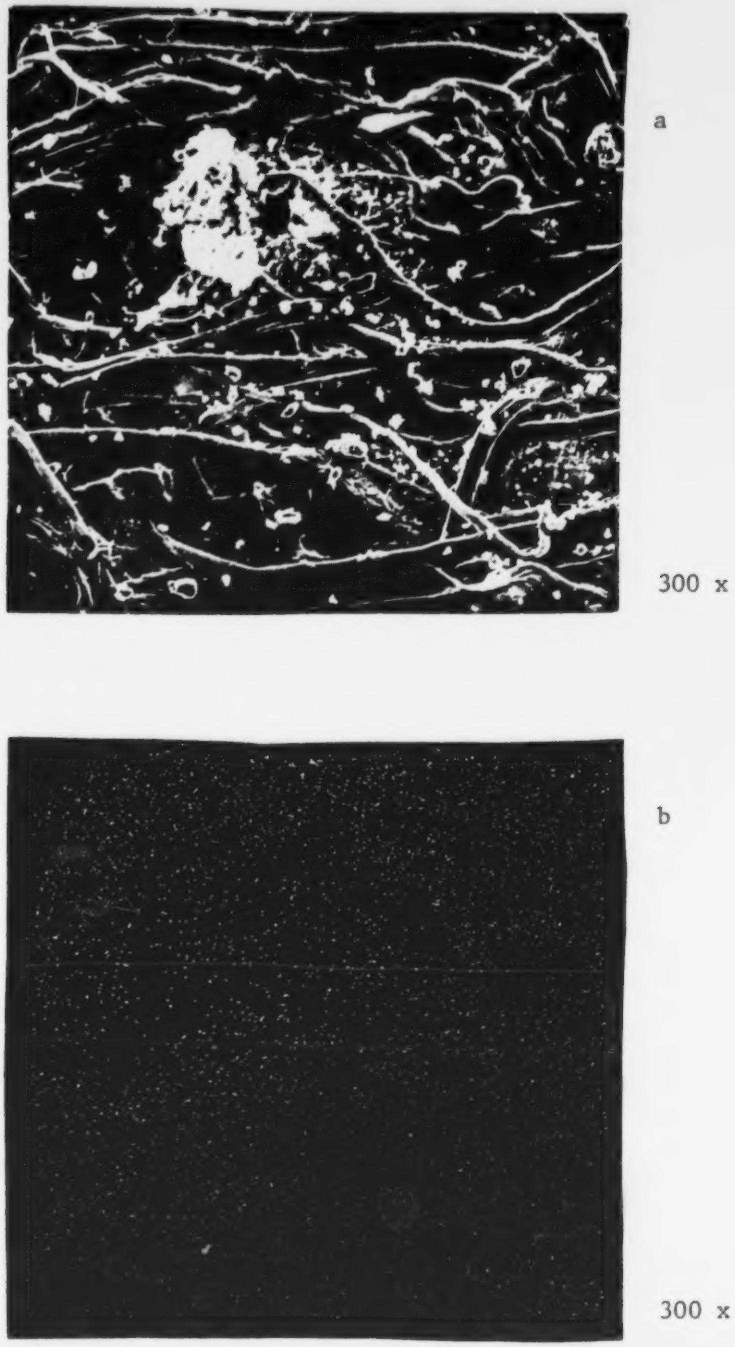


Figure 4.53. (a) Scanning electron micrograph of a region on an air sample collected on a cellulose filter. Sample Volume: 1463.9 m^3. Location - Michigan Chemical Corp., El Dorado, Arkansas. Collected 12/22/76 - 12/23/76; (b) Electron microprobe chlorine map of the region shown in a.

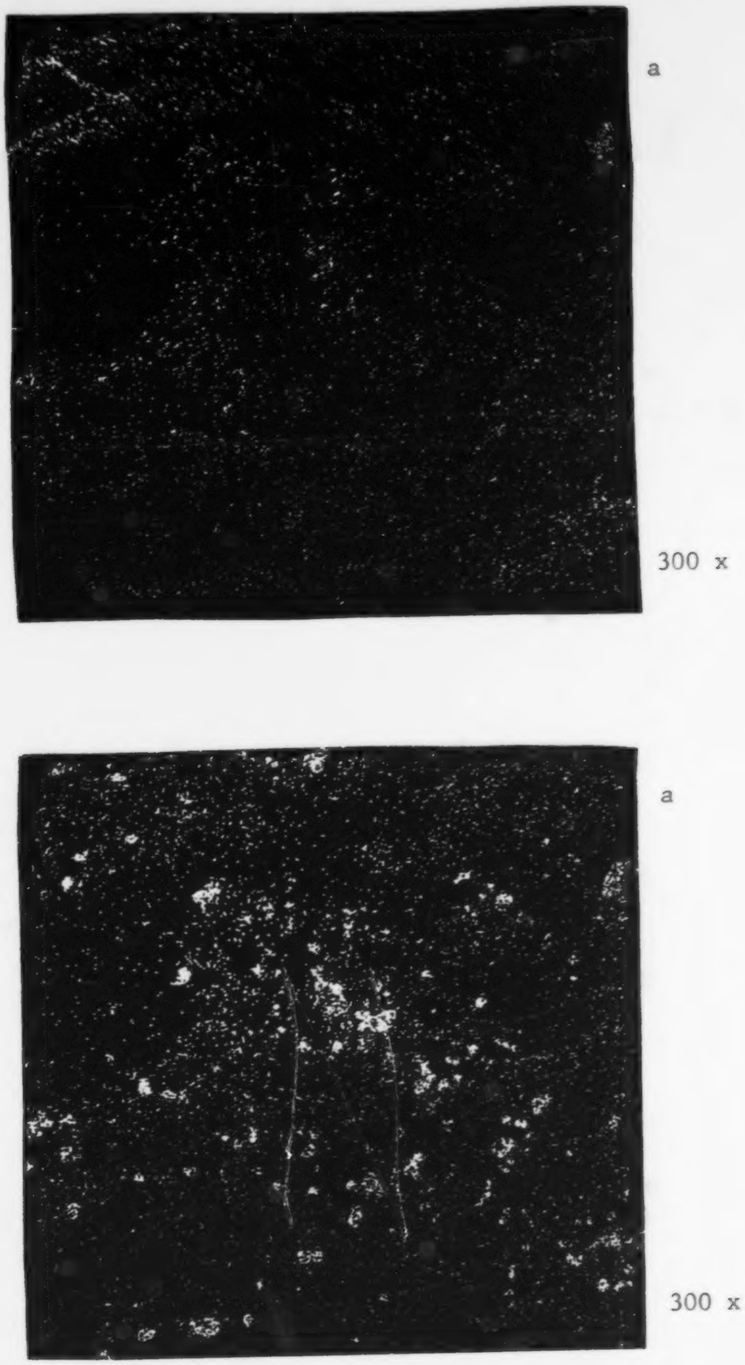

a
300 x
a
300 x

Figure 4.54. Electron microprobe element map of region shown in Figure 4.53.
(a) Aluminum map; (b) Silicon map.

Table 4.30. NEUTRON ACTIVATION ANALYSIS OF AMBIENT AIR HI-VOL SAMPLES

Site	Date	Medium	Br ($\mu g/m^3$)	Cl ($\mu g/m^3$)
MIC[a]	12/19/76-	GFF[b]	2.05	0.91
	12/20/76	CF[c]	0.18	0.062
MIC	12/21/76-	GFF	0.16	0.37
	12/22/76	CF	0.16	0.31
MIC	12/22/76-	GFF	6.23	28.25
	12/23/76	CF	19.6	8.25

[a] All were 24 hr samples.

[b] GFF = glass fiber filter.

[c] CF = cellulose filter.

analyzed by GLC/ECD. The resulting chromatogram for one such sample is shown in Figure 4.55, along with the standard. The chromatograms were surprisingly free of interferences using the described conditions. An evaluation of the completeness of extraction was performed for both glass fiber filter samples and cellulose filters. A second extraction with a fresh 5 ml portion of acetone was performed. The recoveries of 20 and 10% in the second extract for glass fiber and cellulose filters, respectively, are consistent with solvent holdup of each filter. Extraction efficiency was greater than 90% for a single extraction.

The results of the GLC/ECD analysis were negative for TRIS in samples collected from 12/18/76-12/22/76; however, 70 ± 0.12 ng/m^3 and 50 ± 0.11 ng/ m^3 of TRIS were found on glass fiber filter and cellulose filter, respectively, collected from 12/22/76-12/23/76. These must be regarded as minimum values since collection efficiencies and recoveries have not been vigorously established for Hi-Vol filters. The determinations reported above were replicates performed on two days on a different segment of the filters.

GLC/MS/COMP.--Confirmation of the presence of TRIS was achieved by GLC/MS using multiple ion detection. The chromatograms of an extract and a TRIS standard are shown in Figure 4.56 and the peak areas of the selected ions are given in Table 4.31.

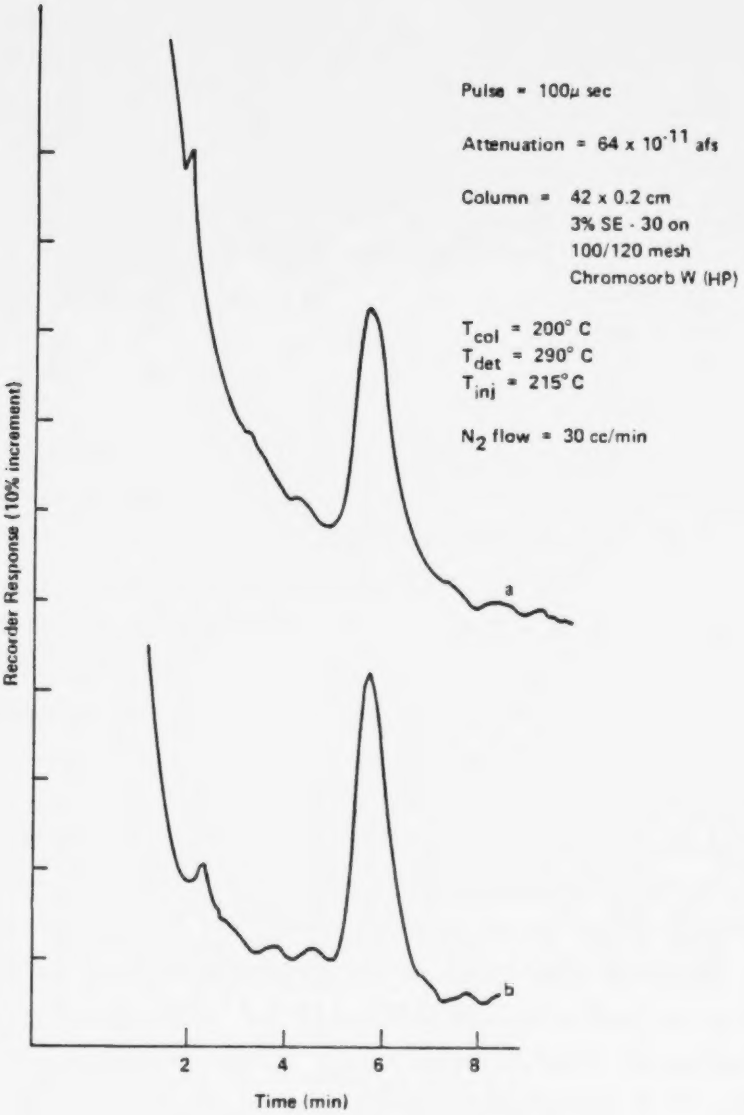


Figure 4.55. Gas liquid chromatography/electron capture detection (^{63}Ni) of (a) an acetone extract of the Hi-Vol glass fiber filter sample collected 12/22/76 - 12/23/76 at Michigan Chemical Corp., El Dorado, AK; and, (b) a TRIS standard (0.8 ng).

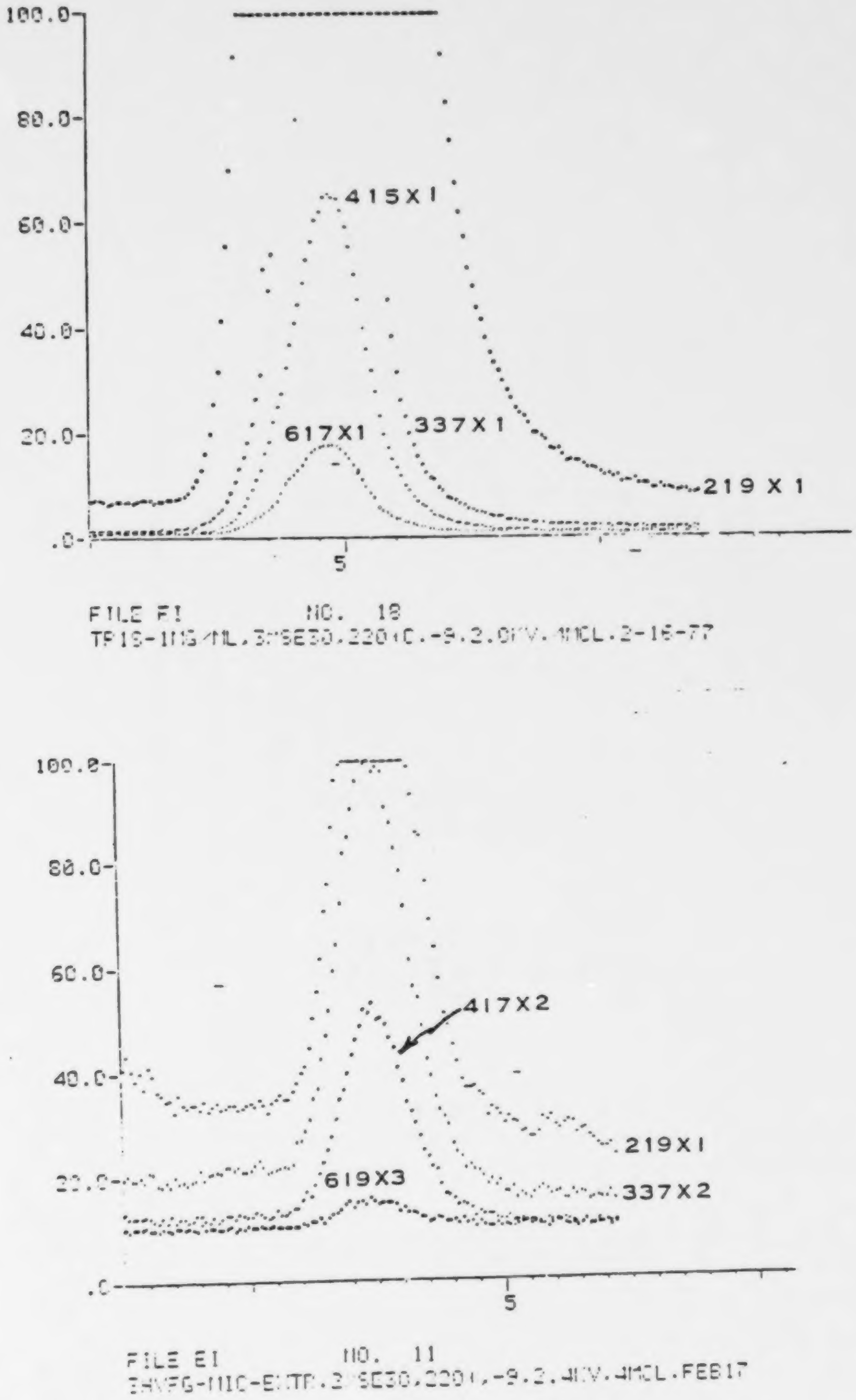


Figure 4.56. Gas chromatography/mass spectrometry analysis with multiple ion detection of (a) TRIS standard and, (b) extract of Hi-Vol glass fiber filter sample collected at Michigan Chemical Company 12/22/76 - 12/23/76.

Table 4.31. PEAK AREAS AND RATIOS OF SELECTED IONS OBTAINED FROM ANALYSIS OF TRIS BY GAS CHROMATOGRAPHY-MASS SPECTROMETRY IN MULTIPLE ION DETECTION MODE

Sample	m/e[a]	RT (min)[b]	Peak Area	Background	Ratio of m/e Values		Ion Ratioed
					Observed	Predicted	
TRIS standard	217	4.69	1150.78	05.18	1.08	1.01	217/219
	219	4.68	1063.84	04.54			
	335	4.69	114.98	01.34	0.52	0.51	335/337
	337	4.63	219.62	01.14			
	415	4.68	37.60	00.90	0.36	0.34	415/417
	417	4.68	103.72	01.00			
	617	4.71	08.72	00.88	0.91	1.02	617/619
	619	4.61	09.46	00.84			
Extract of Hi Vol sample collected at Michigan Chemical Co., 12/22/76-12/23/76 (G.F.F.)	217	4.56[c]	2059.92	26.44	1.09	1.01	217/219
	219	4.61	1888.80	31.54			
	335	4.46	413.10	10.30	0.49	0.51	335/337
	337	4.44	837.44	09.58			
	415	4.48	144.92	07.38	0.36	0.34	415/417
	417	4.48	389.50	06.06			
	617	4.43	36.60	03.46	1.00	1.02	617/619
	619	4.46	36.74	03.44			

a) These m/e values were selected as most characteristic of TRIS.

b) Retention time on gc column (3% SE-30 on Supelcoport 100/120 mesh; 42 x 0.2 cm col; Tcol = 220; flow rate 30 ml/min.

c) Slight variation in retention time represents day to day variation as the retention time for an extract run on the same day was 4.76 ± 0.08 min.

4.2.3.3 Inorganics in Ambient Air

Chloride/Bromide and Chlorine/Bromine.--The results obtained by turbidimetric determination of total halide are given in Table 4.32. The site, period and cycle designation were given in the sampling protocol (Table 4.28) and the locations on the schematic maps (Fig. 4.45).

Table 4.32. CONCENTRATIONS OF HALOGENS AND HALIDES IN AMBIENT AIR SURROUNDING MICHIGAN CHEMICAL CORP. (VELSICOL)[a,b]

Species	Locations			
	L1	L2	L3	L4
Cl_2/Br_2[c]	300 ± 99	293 ± 280	<80	<82
Br_2[d]	<42	<68	<17	<35
Cl^-/Br^-[c]	<69	300 ± 110	<56	<57
Br^-[d]	<21	<34	35	50

[a] Samples are from P1/C3.

[b] Values are in $\mu g/m^3$.

[c] By turbidity.

[d] By neutron activation analysis.

At Michigan Chemical Corp., detectable quantities of halogens were found at L1 (downwind from the holding pond) and L2 (Fig. 4.45). Detectable quantities of halide were found at L2 only. Comparable data for bromine obtained by neutron activation analysis (Table 4.32) indicate the predominant element is probably chlorine and/or chloride. Neutron activation analysis performed on cellulose filters (acid mist) used in sampling immediately following the impinger sampling showed significant amounts of bromine collected at L3 and L4.

Fluoride/Fluorine.--No fluoride or fluorine could be detected in any samples (Table 4.33). The limits of detection were approximately 0.012 ppm in the impinger solution based on the volume of air sampled and the sensitivity of the turbidimetric technique.

Table 4.33. CONCENTRATIONS OF FLUORIDE/FLUORINE IN AMBIENT AIR SURROUNDING MICHIGAN CHEMICAL CORP. (VELSICOL)[a,b]

		Locations			
Period	Cycle	L1	L2	L3	L4
P1	C3	<4.2	<6.7	<3.2	<3.1

[a] Values in $\mu g/m^3$.

[b] Determined by ion specific electrode.

Acid Mist.--No titratable acid was found in any sample. Table 4.34 summarizes the upper limit of ambient air concentration of acid mist.

4.2.3.4 Bromine and Brominated Organics in Brine

Neutron Activation Analysis.--Table 4.35 lists the concentration of bromine (molecular plus halide) in brine samples. A reduction of 90% of the bromine concentration was observed between the front and tail brine. Significant quantities of bromine were still detected in the tail brine samples. However, the technique of neutron activation did not distinguish whether the bromine is present as molecular bromine, bromide ion or brominated organics. Furthermore, the number of bromines per organic molecule could not be delineated by this technique. The importance of these results is primarily attributed to the presence of substantial quantities of "bromine" even after bromine extraction.

GLC/MS/COMP Analysis for Volatile Organics.--Volatile halogenated organics were recovered from water using previously described methods (Appendix A). Figures 4.57 and 4.58 depict the total ion current chromatograms for the volatile organics which were observed in front and tail brine samples. The unequivocal identification of benzene and toluene was established in Michigan Chemical Corp. front brine sample (Fig. 4.57). In the tail brine sample (Fig. 4.58) from the same site we identified bromodichloromethane (Fig. 4.59), toluene, dibromochloromethane (Fig. 4.60) and bromoform.

The halogenated and other organics which were identified and quantitated in brine samples from Michigan Chemical Corp. are shown in Table 4.36. The

Table 4.34. ACID MIST IN AMBIENT AIR SURROUNDING MICHIGAN CHEMICAL CORP. AS H_2SO_4[a]

		Locations			
Period	Cycle	L1	L2	L3	L4
P1	C4	<50	<44	<50	<51

[a] Values as μg/m^3.

Table 4.35. CONCENTRATION OF BROMINE IN BRINE SAMPLES

Site	Sample Type	μg Br/ml
Michigan Chemical Corp.	Front brine	6421.5
	Tail brine	645.8

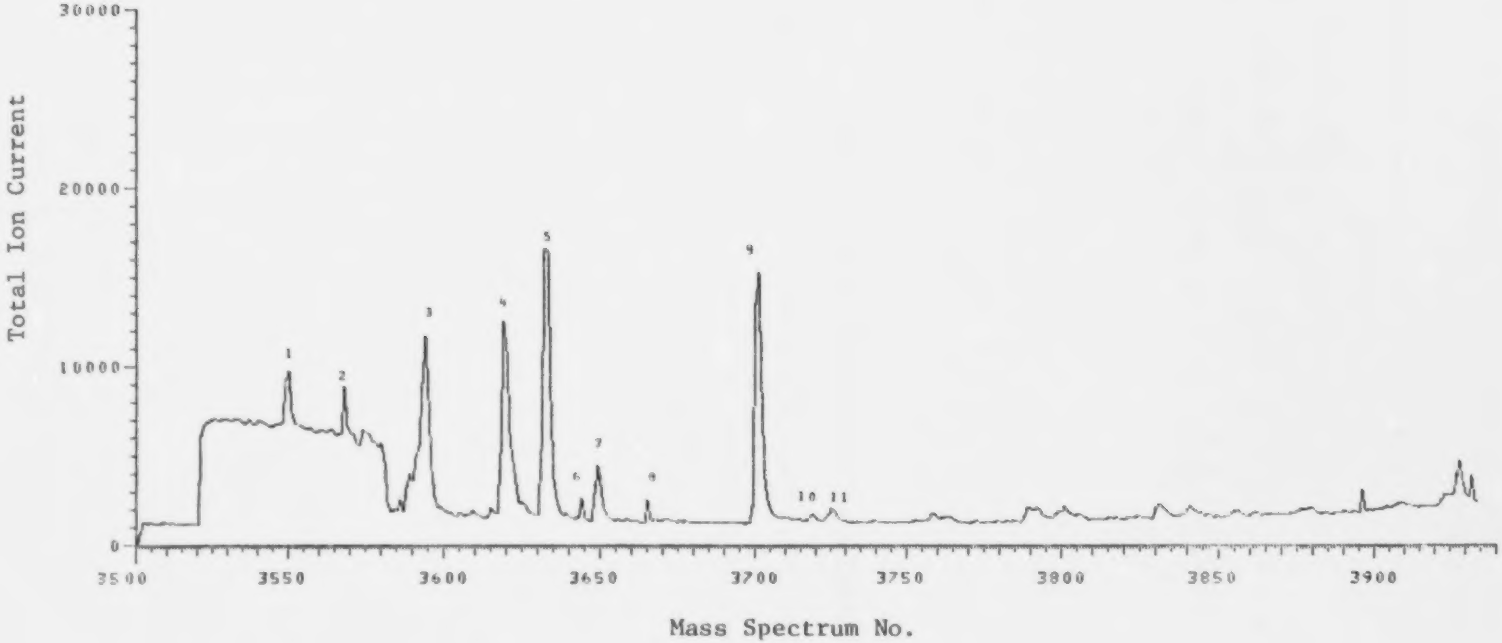


Figure 4.57. Total ion current profile of volatile organics in front brine sample from Michigan Chemical Corp. Peak No. 4 = hexafluorobenzene (es), 5 = perfluorotoluene (es); 7 = benzene and 9 = toluene.

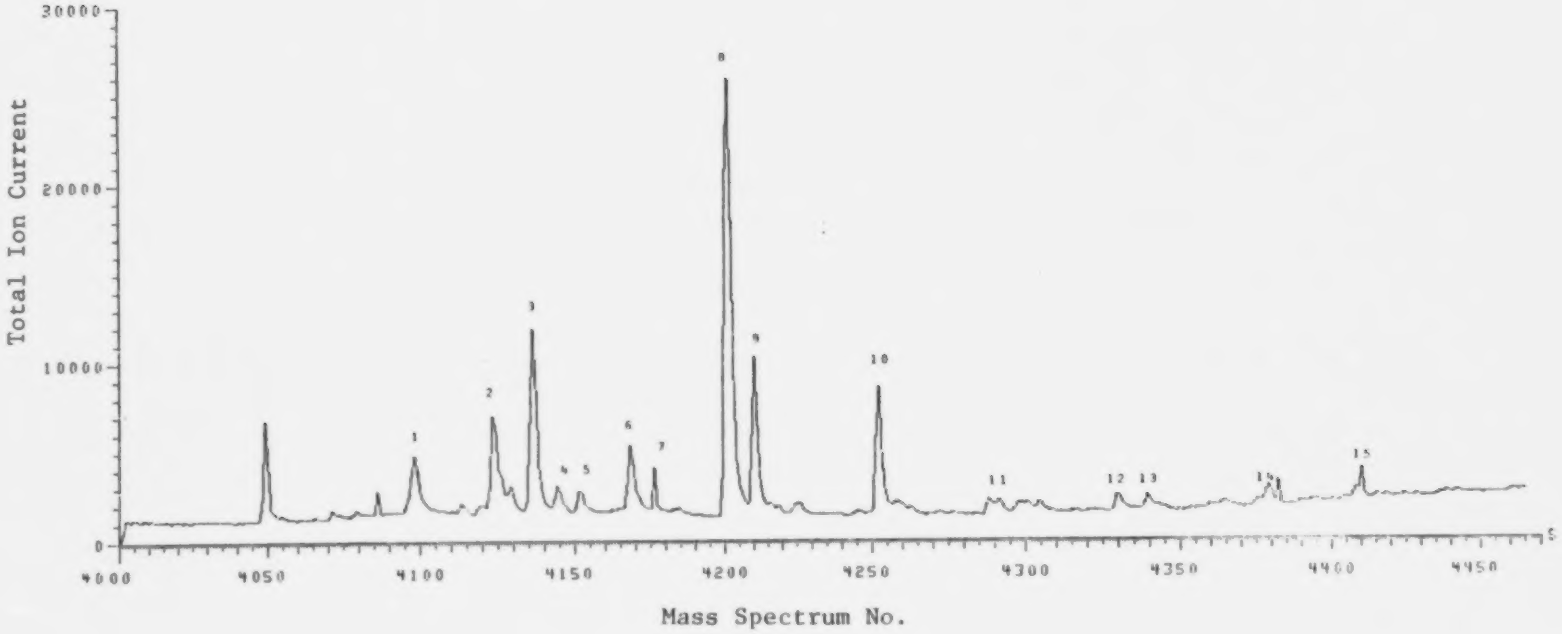


Figure 4.58. Total ion current profile of volatile organics in tail brine sample from Michigan Chemical Corp. Peak No. 2 = hexafluorobenzene (es), 3 = perfluorotoluene (es), 5 = benzene, 6 = bromodichloromethane, 8 = toluene, 9 = dibromochloromethane, and 10 = bromoform.

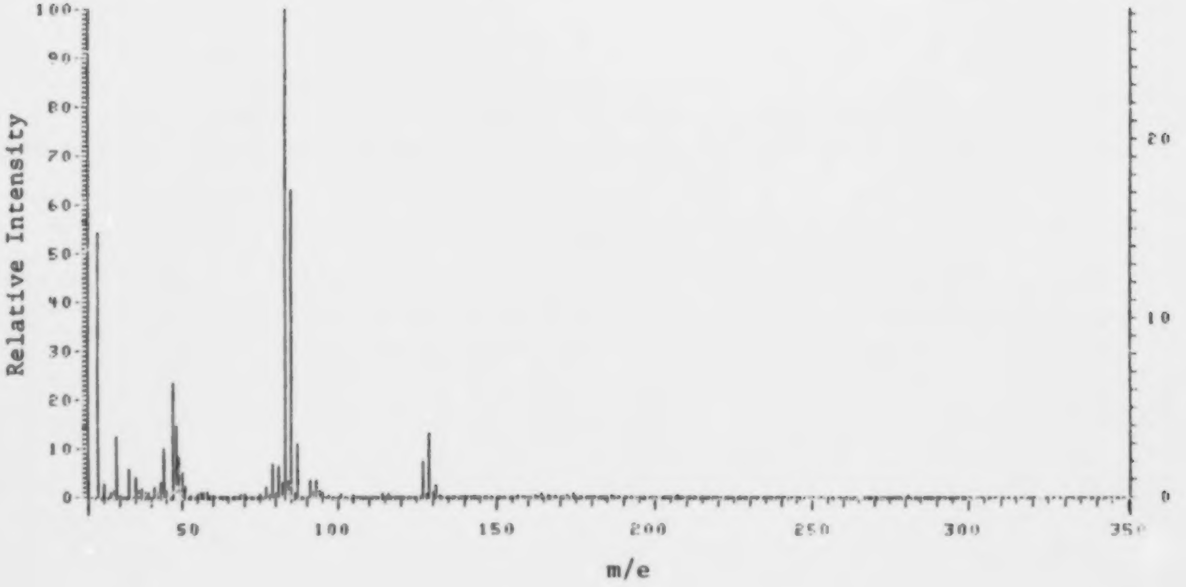


Figure 4.59. Mass spectrum of bromodichloromethane in tail brine sample (MCI). Peak No. 6 in Figure 4.58

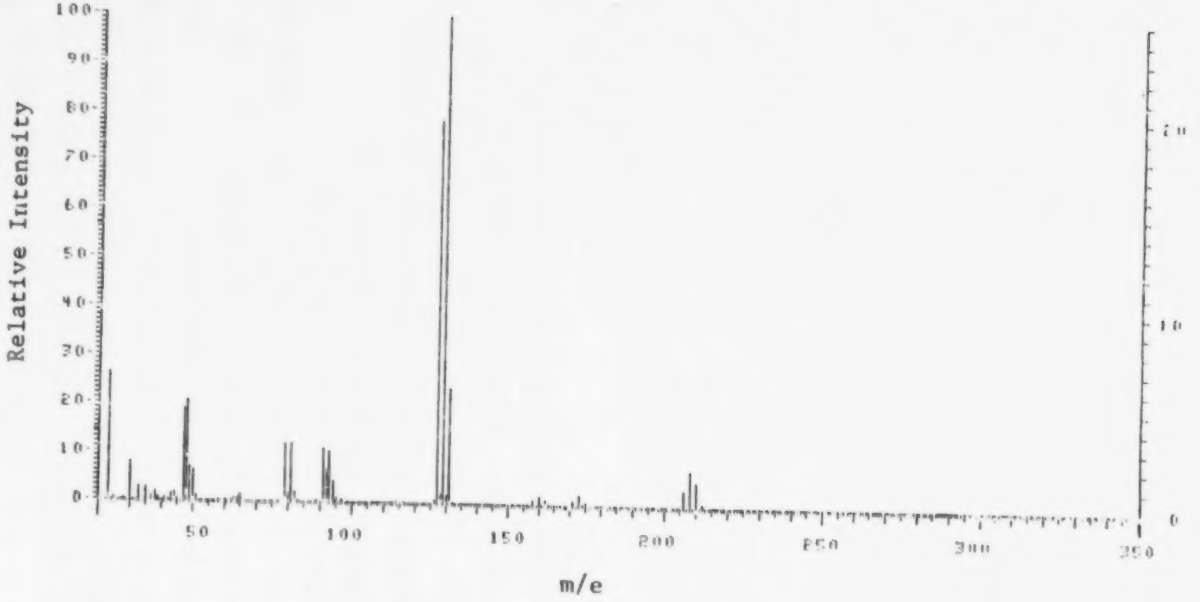


Figure 4.60. Mass spectrum of dibromochloromethane in tail brine sample (MCI). Peak No. 9 in Figure 4.58.

Table 4.36. HALOGENATED AND OTHER ORGANICS IDENTIFIED AND QUANTITATED IN BRINE SAMPLES FROM MICHIGAN CHEMICAL CORP.[a]

Compound	Sample Type	
	Front brine	Tail Brine
Methyl Chloride	5.3	N.D.
Bromoform	8.0	752
Bromodichloromethane	6.7	52
Dibromochloromethane	1.3	800
Hexafluorobenzene (es)[b]	-	-
Perfluorotoluene (es)[b]	-	-
Toluene	1,120	3,200
Benzene	240	120

[a] Concentrations are in ppt.

[b] es = external standard, 200 ng.

concentrations of bromoform, bromodichloromethane and dibromochloromethane were observed to increase significantly after the brine passed through the bromine extraction process.

4.2.3.5 Organic Vapors in Ambient Air

Qualitative Analysis by High Resolution GLC/MS/COMP.--Table 4.37 lists the volatile organics which were identified in ambient air taken from the Michigan Chemical Corp. site. This sample represents the sampling location upwind from the bromine extraction and organic synthesis facilities. The compounds listed in this table are representative of the many components that are generally found in ambient air with the primary contribution from fossil fuel and its combustion. Several halogenated compounds, for example, dichlorodifluoromethane, trichlorofluoromethane, dichloromethane, chloroform, 1,1,1-trichloroethane, carbon tetrachloride and methyl chloride are commonly found as background compounds in ambient air samples taken throughout the Continental United States. Figures 4.61 and 4.62 depict the total ion

Table 4.37. VOLATILE ORGANICS IDENTIFIED IN AMBIENT AIR FROM MICHIGAN CHEMICAL CORPORATION SITE, EL DORADO, ARKANSAS (P1/C1/L1)[a]

Chromatographic Peak No.	Elution Temperature (°C)	Compound
1	40	CO_2
2	41	dichlorodifluoromethane
2A	42	chloromethane
2B	43	1-butene
3	44	acetaldehyde
3A	46	isopentane
4	46	trichlorofluoromethane
5	47	propanal + *n*-pentane + furan
5A	47	C_5H_8 isomer + acetone
5B	48	dimethyl ether + diethyl ether (tent.)
5C	48	dichloromethane
6	49	freon 113 (BKG)
6A		2-methylpropanal
7	53	2-methylpentane
7A	54	crotonaldehyde
7B	54	vinyl acetate (tent.)
8	55	3-methylpentane
8A	55	*n*-butanal
8B	56	methyl vinyl ketone
9	56	methyl ethyl ketone + methylfuran isomer
9A	57	*n*-hexane
10	57	chloroform
10A	59	C_6H_{12} isomer
11	61	methylcyclopentane
11A	62	1,1,1-trichloroethane
11B	64	3-methylbutanal
11C	65	benzene
11D	66	carbon tetrachloride
11E	66	cyclohexane
12	67	2-methylhexane
12A	67	2,3-dimethylpentane
13	68	3-methylhexane
13A	69	C_7H_{14} isomer
14	70	*n*-pentanal
15	72	*n*-heptane
16	77	methylcyclohexane
16A	78	C_8H_{18} isomer
17	83	toluene
18	85	C_8H_{18} isomer
19	87	C_8H_{18} isomer
19A	88	C_8H_{16} isomer
20	89	*n*-hexanal
20A	90	C_8H_{16} isomer
21	92	*n*-octane
21A	97	C_9H_{20} isomer
22	98	C_9H_{20} isomer
22A	99	C_9H_{16} isomer
23	100	C_9H_{20} isomer
24	103	ethylbenzene
25	105	*p*-xylene
26	106	C_9H_{20} isomer
26A	107	C_9H_{20} isomer
26B	108	styrene
27	110	*n*-heptanal
27A	111	C_9H_{18} isomer
28	113	*n*-nonane
29	120	$C_{10}H_{22}$ isomer
29A	120	$C_{10}H_{16}$ isomer
30	121	benzaldehyde
30A	123	C_3-alkyl benzene isomer
31	125	$C_{10}H_{22}$ isomer
32	127	$C_{10}H_{22}$ isomer
32A	129	C_3-alkyl benzene isomer
33	129	*n*-octanal
33A	130	$C_{10}H_{20}$ isomer
34	132	*n*-decane
34A	135	1,2,3-trimethylbenzene
35	138	$C_{11}H_{24}$ isomer
35A	141	C_4-alkyl benzene
36	142	acetophenone
37	144	$C_{11}H_{24}$ isomer
37A	147	unknown
38	149	$C_{11}H_{22}$ isomer + *n*-nonanal
39	151	*n*-undecane
40	162	diethyl phthalate
41	164	decanone isomer
42	166	$C_{12}H_{24}$ isomer
43	168	*n*-dodecane
47	189	*n*-tridecane

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[a] See Table 4.28 for sampling protocol.

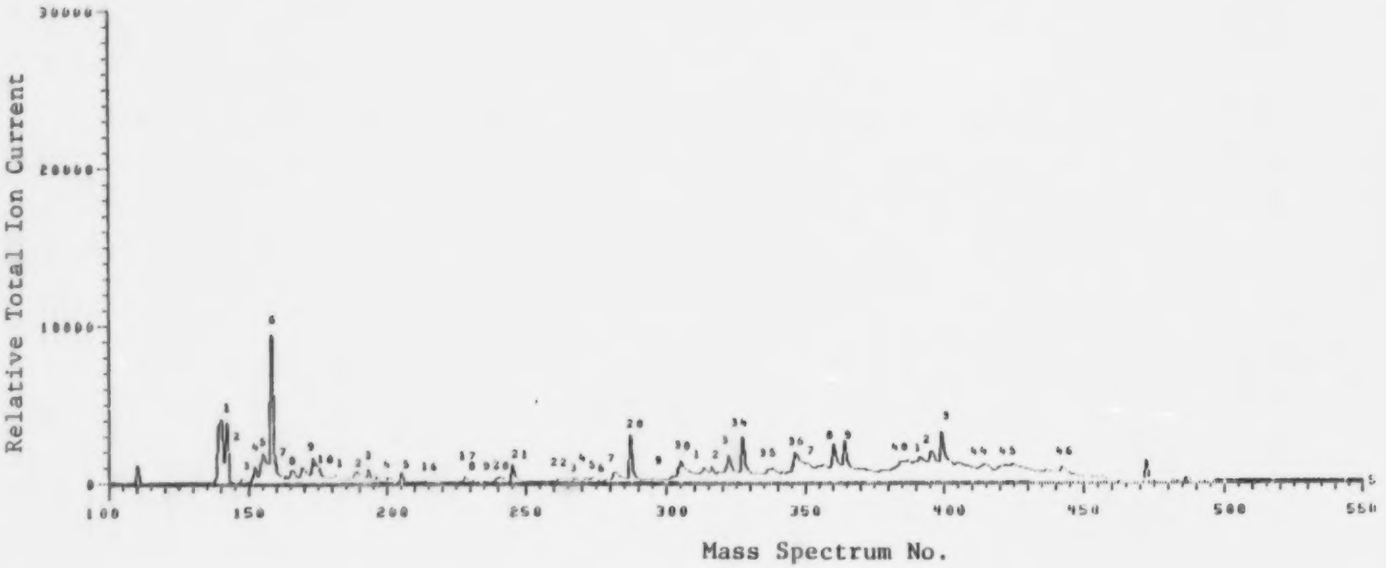

Figure 4.61. Total ion current profile of volatile ambient air pollutants from Michigan Chemical Corp. site, El Dorado, Arkansas (P1/C1/L1).

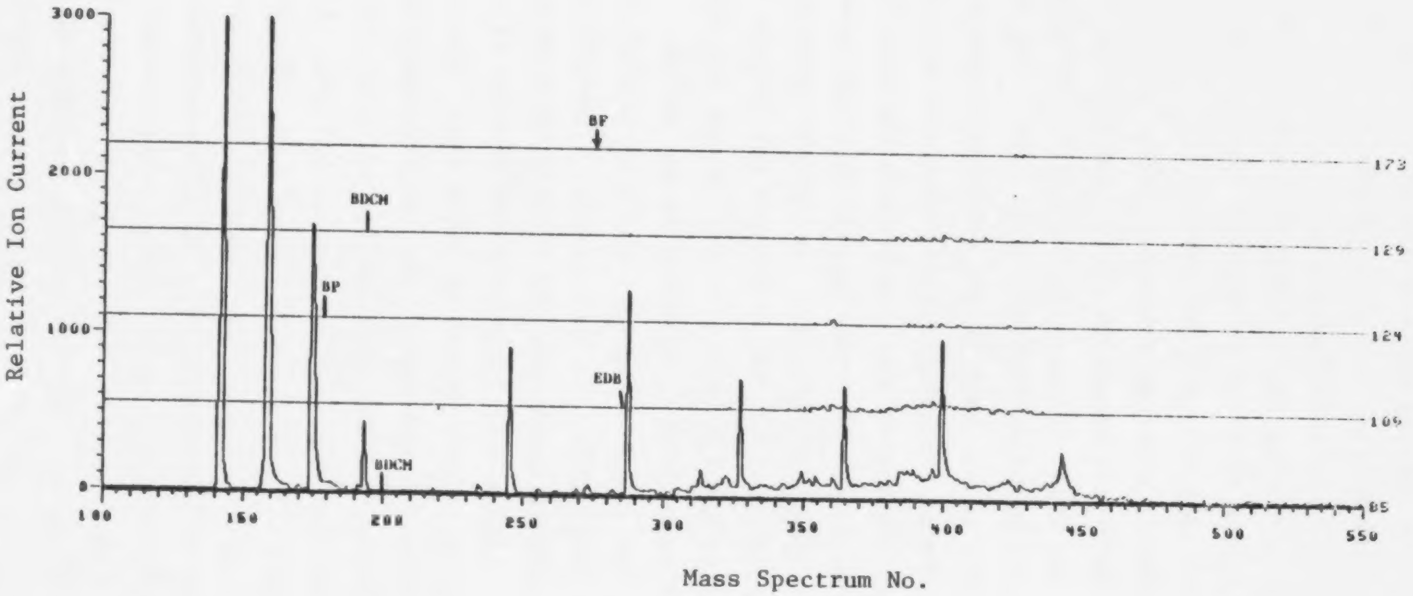

Figure 4.62. Ion chromatograms for ambient air sample from Michigan Chemical Corp. site, El Dorado, Arkansas (P1/C1/L1). BF = bromoform, BP = bromopropane, EDB = ethylene dibromide, BDCM = bromodichloromethane.

current profile and ion chromatogram generated by the GLC/MS/COMP system of the volatile ambient air pollutants which were identified in Table 4.37. The relative total ion current axis is fully attenuated to allow the comparison of overall intensity of the pollution profiles.

In Figure 4.62 ion chromatograms are depicted for the ambient air sample taken from the upwind location at Michigan Chemical Corp. The ions chosen - *m/e* 85, *m/e* 109, *m/e* 124, *m/e* 129 and *m/e* 173 - correspond to bromodichloromethane (BDCM), ethylene dibromide (EDB), bromopropane (BP), bromodichloromethane (BDCM) and bromoform (BF), respectively.

Table 4.38 lists the volatile organics identified in ambient air sample taken at L2 on the Michigan Chemical Corp. site. The sampling location in this case was on the bank of the pond and downwind from the spent brine pond, but upwind from the bromine extraction and organic synthesis facilities. During the entire sampling period, the wind direction was toward the main plant facility. Dibromochloromethane and bromoform were identified. Figure 4.63 depicts the total ion current profile of the volatile ambient air pollutants listed in Table 4.38. Figure 4.64 shows the ion chromatograms for *m/e* 186, *m/e* 173, *m/e* 129 and *m/e* 124. In this figure the peaks which correspond to DBCM and BF are marked.

Table 4.39 lists the volatile organics which were identified at L3 on the Michigan Chemical Corp. site. In this sample, bromomethane, a chlorobromopropene isomer, 1,2-dibromoethane, and 1,1-dibromo-2-bromochloropropane were identified. Figure 4.65 represents the profile of the volatile ambient air pollutants which were listed in Table 4.39. The relatively large peaks (46 and 47) which appeared in this chromatogram could not be identified, however, based upon the mass spectra of these two chromatographic peaks, it was concluded that they did not contain halogen. A series of ion chromatograms for Figure 4.65 is shown in Figure 4.66. The ions at *m/e* 186, *m/e* 109, *m/e* 157, *m/e* 85 and *m/e* 124 represent the external standards, perfluorobenzene and perfluorotoluene, and 1,2-dibromoethane, dibromochloropropane, bromodichloromethane and bromopropane, respectively. The identities of the components of a sample taken at L4 are given in Table 4.40. The relationship of this location to the brine ponds, bromine extraction, and organic synthesis facilities is shown in Figure 4.45. In this sample we

Table 4.38. VOLATILE ORGANICS IDENTIFIED IN AMBIENT AIR FROM MICHIGAN CHEMICAL CORPORATION SITE, EL DORADO, ARKANSAS (P1/C1/L2)[a]

Chromato- graphic Peak No.	Elution Temp. (°C)	Compound
1	39	CO_2
1A	40	dichlorodifluoromethane
1B	41	chloromethane
1C	41	1-butene
1D	42	*n*-butane
1E	44	acetaldehyde
2	45	trichlorofluoromethane
2A	46	C_5H_{10} isomer
2B	46	C_5H_8 isomer
2C	47	isopentane
3	47	acetone + dimethyl ether + diethyl ether (tent.)
3A	48	dichloromethane (tent.)
4	48	freon 113 (BKG)
4A	51	*n*-pentane
5	52	2-methylpentane
5A	53	2-methylpropenal
5B	54	3-methylpentane
5C	54	*n*-butanal
6	55	hexafluorobenzene (e§)
6A	56	*n*-hexane
7	56	chloroform
7A	57	methyl ethyl ketone
8	59	perfluorotoluene (e§)
8A	60	methycyclopentane
8B	61	1,1,1-trichloroethane
9	63	benzene
9A	64	carbon tetrachloride
10	65	2-methylhexane
10A	66	2,3-dimethylpentane
10B	67	3-methylhexane
10C	68	C_7H_{14} isomer
11	69	3-methylbutanal + C_7H_{14} isomer
11A	70	bromodichloromethane
11B	71	*n*-pentanal
12	71	*n*-heptane
13	76	methylcyclohexane
14	78	4-methyl-2-pentanone
15	83	toluene
16	85	C_8H_{18} isomer
17	80	dibromochloromethane
17A	87	C_8H_{16} isomer
18	89	*n*-hexanal + C_8H_{16} isomer
19	91	*n*-octane
19A	92	tetrachloroethylene
19B	93	C_8H_{16} isomer
20	102	ethylbenzene
20A	103	C_9H_{20} isomer
21	104	*p*-xylene
21A	105	bromoform
21B	106	C_9H_{20} isomer
22	107	C_9H_{20} isomer
22A	108	styrene
23	109	*o*-xylene
23A	110	C_9H_{18} isomer
23B	111	heptanal
24	112	*n*-nonane
24A	116	$C_{10}H_{22}$ isomer
24B	118	$C_{10}H_{20}$ isomer
25	120	$C_{10}H_{22}$ isomer
25A	121	C_9H_{18} isomer
26	121	benzaldehyde
27	123	*p*-ethyltoluene
28	125	$C_{10}H_{22}$ isomer
29	127	$C_{10}H_{22}$ + C_3-alkyl benzene isomers
29A	129	methylheptanal isomer
30	130	*n*-octanal
30A	131	$C_{10}H_{20}$ + C_3-alkyl benzene isomers
31	132	*n*-decane
31A	134	$C_{11}H_{24}$ isomer
31B	135	C_4-alkyl benzene isomer
32	137	$C_{11}H_{24}$ isomer
33	142	acetophenone
34	144	cresol isomer
34A	145	$C_{11}H_{24}$ isomer
34B	147	$C_{11}H_{22}$ isomer
35	149	*n*-nonanal
35A	150	$C_{11}H_{22}$ isomer
36	151	*n*-undecane
37	154	$C_{12}H_{26}$ isomer
37A	155	$C_{10}H_{26}$ isomer
38	156	dimethylphenol isomer
38A	160	$C_{12}H_{26}$ isomer
39	177	$C_{12}H_{26}$ isomer
40	179	$C_{13}H_{28}$ isomer
40B	185	$C_{13}H_{28}$ isomer
40C	188	$C_{14}H_{30}$ isomer

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[a] See Table 4.27 for sampling protocol.

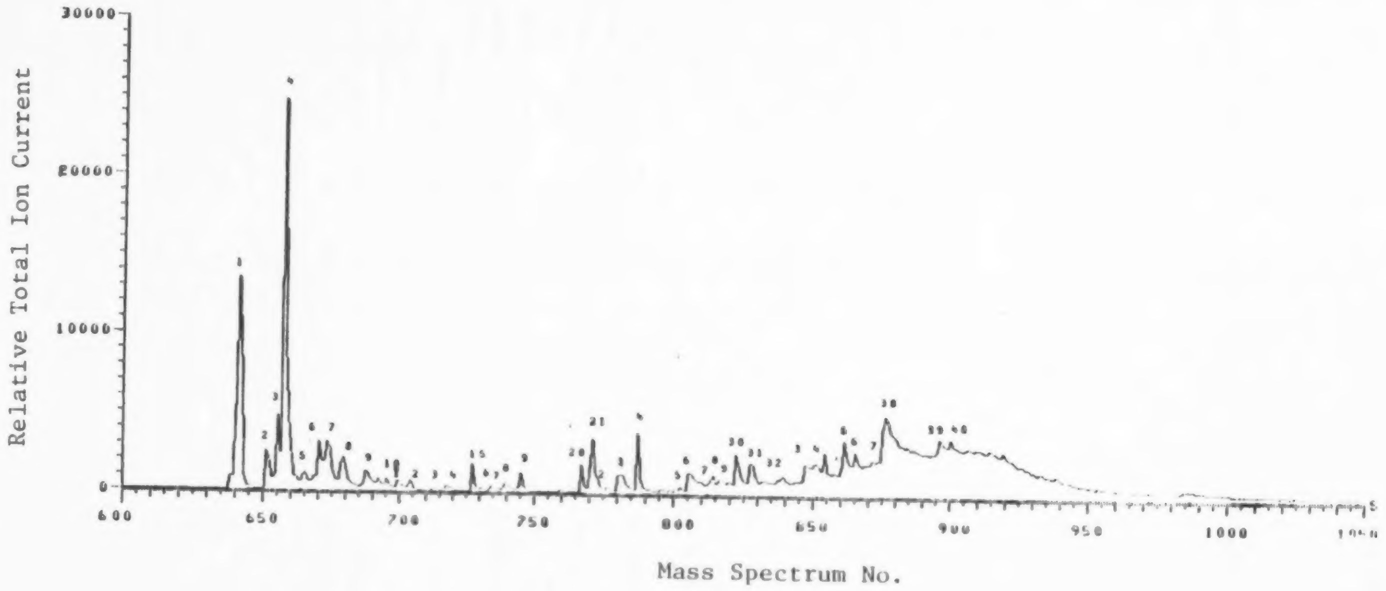


Figure 4.63. Total ion current profile of volatile ambient air pollutants from Michigan Chemical Corp. site, El Dorado, Arkansas (P1/C1/L2).

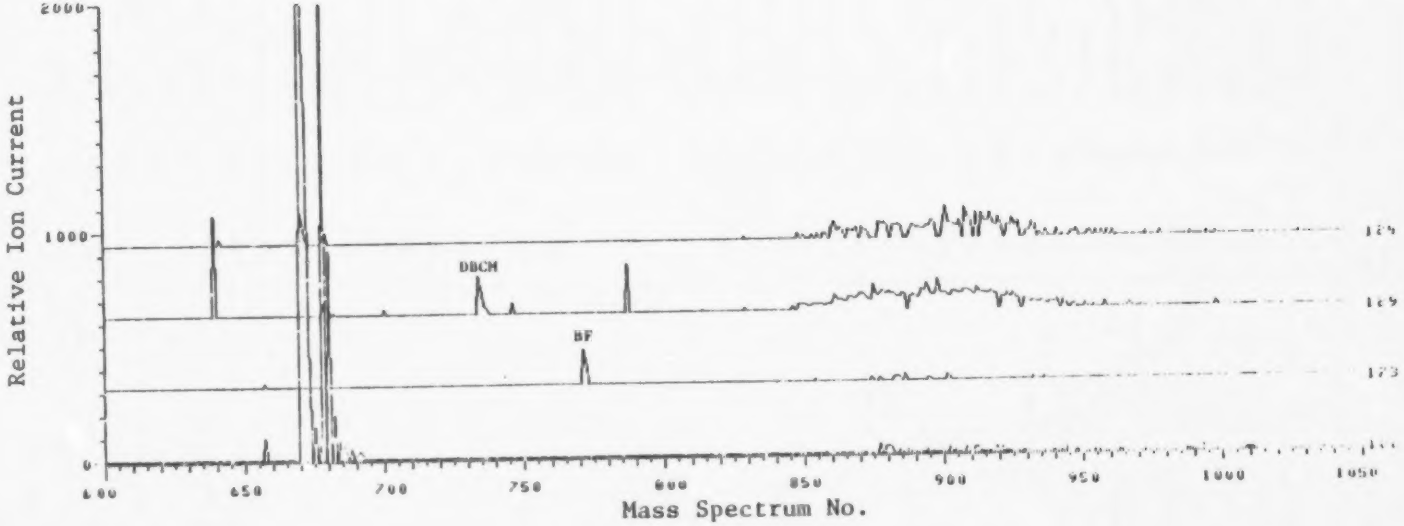


Figure 4.64. Ion chromatograms for ambient air sample from Michigan Chemical Corp. site, El Dorado, Arkansas (P1/C1/L2). BF = bromoform, DBCM = dibromochloromethane.

Table 4.39. VOLATILE ORGANICS IDENTIFIED IN AMBIENT AIR FROM MICHIGAN CHEMICAL CORPORATION SITE, EL DORADO, ARKANSAS (P1/C1/L3)[a]

Chromato-graphic Peak No.	Elution Temp. (°C)	Compound
1	39	CO_2
1A	41	dichlorodifluoromethane
1B	43	1-butene + *n*-butane
2	43	acetaldehyde
2A	44	bromomethane
3	46	trichlorofluoromethane
4	47	C_5H_{10} isomer
4A	47	propanal + propenal + furan
5	48	acetone
5A	48	C_5H_8 isomer
5B	49	dichloromethane
6	50	freon 113 (BKG)
6A	52	*n*-pentane
6B	53	2-butenal
7	54	2-methylpentane
7A	55	2-methylpropenal
8	56	*n*-butanal + 3-methylpentane
9	57	hexafluorobenzene (eS)
10	58	*n*-hexane
11	59	chloroform
11A	61	methyl ethyl ketone
12	62	perfluorotoluene (eS)
14	66	benzene
14A	66	carbon tetrachloride
14B	67	cyclohexane
15	68	2-methylhexane
15A	69	2,3-dimethylpentane
16	70	3-methylhexane
16A	70	C_6H_8 isomer
17	71	3-methylbutanal
17A	73	*n*-pentanal
18	74	*n*-heptane
18A	75	C_7H_{14} isomer
18B	75	C_7H_{14} isomer
19	81	$C_6H_{12}O$ isomer
20	86	toluene
21	88	C_8H_{18} isomer + chlorobromopropene isomer (tent.)
22	89	C_8H_{18} isomer
22A	91	2-methylpentanal
22B	91	C_8H_{16} isomer
23	92	*n*-hexanal
23A	92	dibromoethane
23B	93	C_8H_{18} isomer
23C	93	C_8H_{16} isomer
24	94	*n*-octane
25	95	tetrachloroethylene
25A	98	C_9H_{20} isomer
25B	99	C_8H_{16} isomer
25C	99	C_9H_{20} isomer
26	104	ethylbenzene
27	106	*p*-xylene
27A	107	C_9H_{20} isomer
28	108	C_9H_{20} isomer
28A	109	2-heptanone
29	110	styrene
30	111	*o*-xylene + *n*-heptanal
30A	112	C_9H_{18} isomer
31	114	*n*-nonane
31A	116	C_9H_{18} isomer
31B	118	isopropylbenzene
31C	119	$C_{10}H_{22}$ isomer
31D	120	$C_{10}H_{22}$ isomer
32	121	propylcyclohexane
32A	122	$C_{10}H_{16}$ isomer
33	123	benzaldehyde + $C_{10}H_{22}$ isomer
33A	124	*n*-propylbenzene
34	125	*p*-ethyltoluene
35	126	$C_{10}H_{22}$ isomer
36	127	$C_{11}H_{24}$ isomer
37	128	$C_{10}H_{22}$ isomer
37A	129	$C_{10}H_{22}$ isomer
37B	130	$C_{10}H_{20}$ isomer
38	131	octanal
38A	131	*o*-ethyltoluene
38B	132	$C_{10}H_{20}$ isomer
39	133	*n*-decane
39A	135	$C_{10}H_{20}$ isomer
40	136	1,2,3-trimethylbenzene
40A	136	C_4-alkyl benzene isomer
40B	137	$C_{11}H_{24}$ isomer
40C	137	$C_{10}H_{20}$ isomer
41	138	$C_{11}H_{24}$ isomer
41A	139	$C_{10}H_{20}$ isomer
41B	140	$C_{11}H_{24}$ isomer
41C	141	C_4-alkyl benzene isomer
41D	141	$C_{11}H_{24}$ isomer

(continued)

Table 4.39 (cont'd)

Chromato-graphic Peak No.	Elution Temp. (°C)	Compound	Chromato-graphic Peak No.	Elution Temp. (°C)	Compound
41E	142	C_4-alkyl benzene isomer	45	151	*n*-undecane
42	143	$C_{11}H_{24}$ + 1,1-dibromo-2-chloropropane	45A	152	$C_{12}H_{26}$ isomer
43	145	$C_{11}H_{24}$ isomer	46	212	unknown
44	149	$C_{11}H_{22}$ isomer	47	217	unknown

[a] See Table 4.28 for sampling protocol.

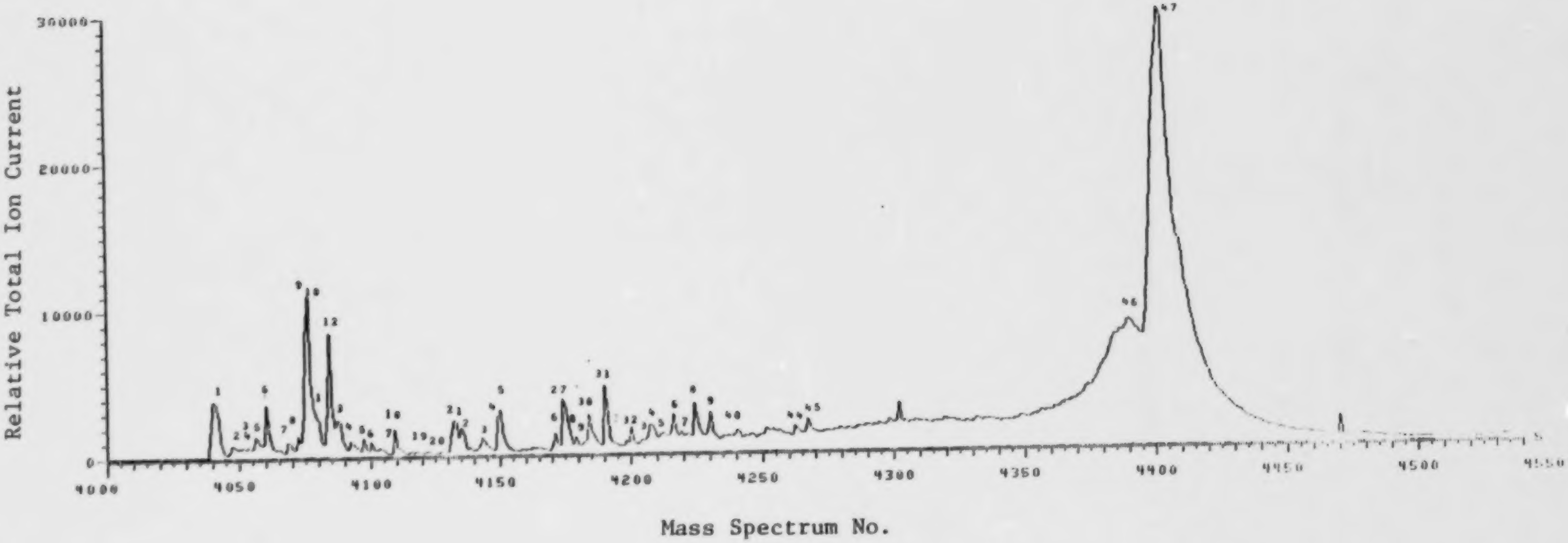


Figure 4.65. Total ion current profile of volatile ambient air pollutants from Michigan Chemical Corp. site, El Dorado, Arkansas (P1/C1/L3).

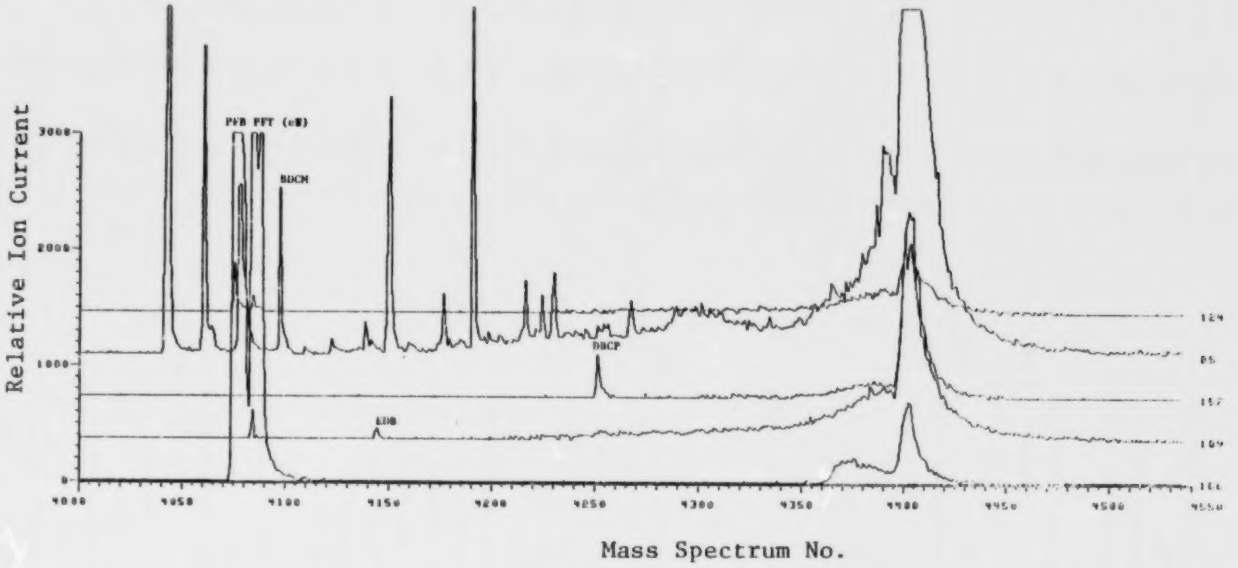


Figure 4.66. Ion chromatograms for ambient air sample from Michigan Chemical Corp. site, El Dorado, Arkansas (P1/C1/L3). BDCM = bromodichloromethane, EDB = ethylene dibromide, DBCP = 1,1-dibromo-2-chloropropane.

Table 4.40. VOLATILE ORGANICS IDENTIFIED IN AMBIENT AIR FROM MICHIGAN CHEMICAL CORPORATION SITE, EL DORADO, ARKANSAS (P1/C1/L4)[a]

Chromato-graphic Peak No.	Elution Temp. (°C)	Compound
1	39	CO_2
3	41	dichlorodifluoromethane
4	42	1-butene
4A	43	bromoethane (tent.)
5	44	acetaldehyde
5A	45	isopentane
6	46	trichlorofluoromethane
6A	46	propenal + propanal + furan
7	47	*n*-pentane + C_5H_8 isomer
7A	47	acetone
8	49	dichloromethane + freon 113 (BKG)
8A	51	2-methylpropenal
9	53	2-methylpentane
9A	54	2-methylpropenal
10	55	3-methylpentane
10A	55	*n*-butanal
11	56	hexafluorobenzene (eS)
11A	57	*n*-hexane
11B	58	chloroform
11C	59	methyl ethyl ketone
11D	59	bromopropane isomer (tent.)
12	60	perfluorotoluene (eS)
12A	61	methylcyclopentane
13	62	1,1,1-trichloroethane
13A	62	allyl bromie
14	64	benzene
14A	65	carbon tetrachloride
14B	65	cyclohexane
15	66	2-methylhexane
15A	67	2,3-dimethylpentane
16	67	3-methylhexane
17	69	*n*-pentanal
18	72	*n*-heptane
20	77	methylcyclohexane
21	79	4-methyl-2-pentanone
22	84	toluene
23	85	chlorobromopropene isomer (tent.) + C_8H_{18} isomer
24	87	3-methylheptane
24A	88	C_8H_{16} isomer
25	89	2-methylpentanal + diisobutylene
26	90	*n*-hexanal
26A	90	dibromoethane isomer
26B	92	C_8H_{16} isomer
27	93	*n*-octane
28	94	tetrachloroethylene
29	100	C_9H_{20} isomer
29A	100	ethylcyclohexane
29B	101	dibromopropane isomer
30	102	1-chloro-3-bromopropane
31	104	ethylbenzene
31A	105	$C_{10}H_{22}$ isomer
32	106	*p*-xylene
33	107	C_9H_{20} isomer
34	108	C_9H_{20} isomer
35	110	styrene + 2,4-dimethylpentanal
36	111	*o*-xylene
36A	111	*n*-heptaldehyde
36B	112	C_9H_{18} isomer
37	114	*n*-nonane
37A	116	C_9H_{18} isomer
37B	117	isopropylbenzene
38	118	$C_{10}H_{22}$ isomer
39	119	$C_{10}H_{22}$ isomer
40	120	propylcyclohexane
41	121	$C_{10}H_{22}$ + $C_{10}H_{16}$ isomers
42	123	benzaldehyde
42A	123	*n*-propylbenzene
43	125	*p*-ethyltoluene
43A	126	$C_{10}H_{22}$ isomer
44	127	$C_{10}H_{22}$ isomer
45	128	C_3-alkyl benzene isomer
46	130	dimethylhexanal or $C_8H_{16}O$ isomer
47	131	*n*-octanal
47A	132	C_3-alkyl benzene isomer
47B	133	C_3-alkyl benzene isomer
47C	133	$C_{10}H_{20}$ isomer
48	134	*n*-decane
49	136	$C_{10}H_{16}$ isomer
50	137	C_4-alkyl benzne isomer
50A	139	$C_{11}H_{24}$ isomer
51	140	$C_{11}H_{24}$ isomer
52	141	$C_{11}H_{22}$ isomer
53	142	C_4-alkyl benzene isomer
54	144	C_4-alkyl benzene isomer
55	145	1-chloro-2,3-dibromopropane
56	147	C_4-alkyl benzene isomer
57	149	C_9-alkyl aldehyde isomer
58	150	*n*-nonanal

(continued)

Table 4.40 (cont'd)

Chromatographic Peak No.	Elution Temp. (°C)	Compound	Chromatographic Peak No.	Elution Temp. (°C)	Compound
58A	152	$C_{11}H_{22}$ isomer	62	167	$C_{12}H_{24}$ isomer
59	153	_n_-undecane	62A	169	$C_{12}H_{26}$ isomer
61	163	dimethylphenol isomer			

[a] See Table 4.28 for sampling protocol.

identified bromomethane, bromopropane, allyl bromide, chlorobromopropene, 1,2-dibromoethane, a dibromopropane isomer, 1-chloro-3-bromopropane and 1-chloro-2,3-dibromopropane. In all of the samples which contained bromopropane, we were unable to determine whether it was a 1- or 2-bromopropane (identical mass spectra) since the authentic material was not available to us for establishing the chromatographic retention time.

Table 4.41 summarizes the halogenated hydrocarbons which were identified by GLC/MS/COMP in ambient air surrounding the Michigan Chemical Corp. plant site.

Table 4.41. HALOGENATED HYDROCARBONS IDENTIFIED BY GC-MS-COMP IN AMBIENT AIR AT MICHIGAN CHEMICAL CORPORATION, EL DORADO, ARKANSAS

Compound	Compound
Allyl Bromide	1-Chloro-3-bromopropane
Bromobenzene	1-Chloro-2,3-dibromopropane
Bromodichloromethane	Dibromochloromethane
Bromoform	1,1-Dibromo-2-Chloropropane
1- or 2-Bromopropane	1,2-Dibromomethane
Bromopropene	Dibromopropane
Chlorobromopropene	Methyl Bromide
	Methyl Chloride

Quantification of Halogenated Hydrocarbons.--Table 4.42 lists the halogenated hydrocarbons which were identified and quantitated in ambient air surrounding the Michigan Chemical Corp. site. In this case, the concentrations were generally in the ng/m^3 range. The highest detected was chlorobromopropene at L5 where a personal sampler was placed at an elevation of 15 feet from ground level. This location was between two buildings which provided a wind corridor coming directly from the organic synthesis facilities. The sampler was approximately 100 meters from that facility. At L4, another

Table 4.42. HALOGENATED HYDROCARBONS IDENTIFIED AND QUANTITATED IN AMBIENT AIR SURROUNDING MICHIGAN CHEMICAL CORP., EL DORADO, AK

Period/Cycle/Location[a]	Allyl bromide	Bromobenzene	Bromodichloromethane	Bromoform	1- or 2-Bromopropane	Chlorobromopropane	1-Chloro-2,3-Dibromopropane	1-Chloro-3-bromopropane	1-Chloro-2,3-Dibromopropane or 1,1-Dibromo-2-chloropropane	Dibromochloromethane	1,1-Dibromo-2-chloropropane	1,2- or 1,3-Dibromopropane	Ethylene dibromide	Methyl bromide
P1/C1/L1	–[b]	–	–	–	–	–	–	–	–	–	–	–	–	–
L2	–	–	6.4	26.4	T[c]	–	–	–	–	7.2	–	–	–	–
L3	–	–	5.2	–	47.2	–	–	–	–	–	2.6	–	1.7	–
L4	T	–	–	–	T	T	–	2.0	17	–	–	1.1	34	T
P1/C2/L2	3.2	–	–	T	20.8	–	–	T	5.4	–	–	–	–	–
L4	–	–	–	–	24.8	–	–	–	6.5	39.8	–	–	–	–
L4 (ELV)	32.9	–	–	–	35	4	20.6	63	–	–	–	–	T	T
L5 (ELV)	–	28	–	4.0	T	83	–	–	–	–	–	–	–	–

[a] See Table 4.28 for sampling protocol, values are in ng/m^3.

[b] – = not detected.

[c] T = trace detected.

DuPont personal sampler was approximately 10 feet from ground level, whereas the remaining samplers were approximately 4 feet above ground.

Estimation of Methyl Chloride, Methyl Bromide, Vinyl Chloride and Vinyl Bromide.--None of these chemicals were detected in ambient air by GC/ECD or mass fragmentography. The LOD of methyl chloride and methyl bromide was 200 and 120 μg/m^3 by GC/ECD.

Ethylene.--The levels of ethylene determined at the Michigan Chemical Corp. site are given in Table 4.43. The observed concentrations were generally regarded as background quantities.

Table 4.43. ETHYLENE LEVELS IN AMBIENT AIR

Site[a]	Period/Cycle/Location	ppm
MCI	P1/C4/L1	0.85 ± 0.15
	P1/C4/L2	0.85 ± 0.05
	P1/C4/L3	0.80 ± 0
	P1/C4/L4	0.75 ± 0.05
	P1/C4/L5	0.85 ± 0.05
	P1/C4/L6	0.85 ± 0.05

[a] See Table 4.28 and Figure 4.45 for sampling protocol and locations.

4.2.3.6 Brominated Organics in Soil and Water

The soil and water samples were screened for EDB and other volatile brominated organics by the VOA method. None were found in any of these samples. The soil sample P1/C1/L1 was extracted and analyzed for semi-volatile brominated organics by direct probe high resolution mass spectrometry and GC/MS/COMP. The results are given in Table 4.44.

Table 4.44. ANALYSIS OF A SOIL SAMPLE FROM THE VICINITY OF MICHIGAN CHEMICAL CORPORATION

Period/Cycle/Location	Decabrom (μg/kg)	Tetrabrom (μg/kg)
P1/C1/L1	ND[a]	1,100[a]

[a] Quantitation by GC/MS/COMP-MID.

4.2.4 Ethyl Corporation

4.2.4.1 Sampling

The sampling protocol and sample descriptions for Ethyl Corp. are given in Table 4.45. The corresponding Figure 4.67 designates the sampling locations for September 23, 1976. Table 4.46 and Figure 4.68 present the protocol and locations for May 17, 1977.

4.2.4.2 Inorganics in Ambient Air

Chloride/Bromide and Chlorine/Bromine.--The results obtained by the turbidimetric determination of a total halide are given in Table 4.47. The site, period and cycle designation were given in the sampling protocols (Table 4.45) and the locations on schematic map (Fig. 4.67). No detectable halogens and halides were observed in samples of ambient air surrounding Ethyl Corp.

Fluoride/Fluorine.--No fluoride or fluorine could be detected in any samples. The limit of detection was less than 2.7 $\mu g/m^3$ based on the volume of air sampled and the sensitivity of the ion selective electrode.

Acid Mist.--No titratable acid was found in any samples. The upper limit of ambient air concentration of acid mist was 41 $\mu g/m^3$ when standardized as H_2SO_4.

4.2.4.3 Organic Vapors in Ambient Air

Qualitative Analysis by High Resolution GC/MS/COMP.--Sampling locations 2 and 3 were 200-250 yards from the bromine extraction and organic synthesis facilities. Location 1 represented an upwind sample near a large storage tank area (see Fig. 4.67 for sampling locations). Figure 4.69 depicts the total ion current profile of the volatile organic pollutants collected at L2 on the Ethyl Corp. site. The large peak (No. 19) was identified as toluene

Table 4.45. SAMPLING PROTOCOL FOR ETHYL CORPORATION, HIGHWAY 79, MAGNOLIA, ARKANSAS

Period	Cycle	Location	Sampling Time	Sampling Volume (ℓ)	Type of Sample	Meteorological Conditions			
						T (°C)	% RH	Wind Dir./ Speed (kmol)	Other
9/23/76 P1	C1	L1	1427-1726	143	HHC[a]	24-30	40-70	180/4-calm	Clear
		L2	1427-1726	140	HHC[a]				
		L3	1422-1726	197	HHC[a]			8-13	Clear, slight Br_2 + H_2S odor
	C2	L4	1355-1903		HHC[b]				
	C3	L1	1729-1830	50.9	F, CBN, CBD				
		L2	1729-1830	28.3	F, CBN, CBD				
		L3	1729-1830	70.8	F, CBN, CBD				Clear
	C4	L1	1835-1944	11	AM				
		L2	1834-1944	115	AM				
		L3	1832-1944	115	AM				
		L4	1508	1	TED				
		L5	1502	1	TED				
		L6	1512	1	TED				
		L7	1517	1	TED				
		L5	1502	0.28	VAC				

[a] Nutech Model 220 sampler 3-6 ft elevation.

[b] DuPont sampler 3-6 ft elevation.

Locations shown in Figure 10.

Key to Sample Type:

HHC - Halogenated Hydrocarbon
F - Fluorine and Fluoride
CBN - Bromine and Chlorine
CBD - Bromide and Chloride
AM - Acid Mist
TED - Tedlar Bag
VAC - Aluminum Vacuum Can

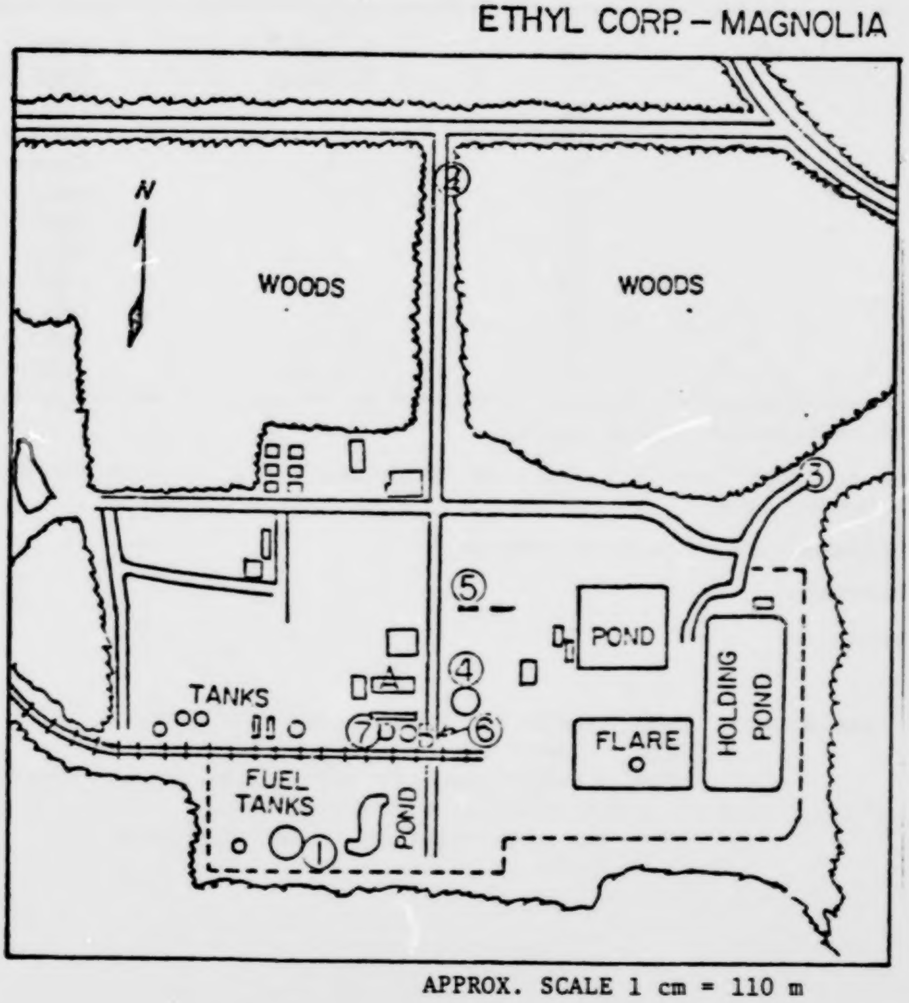

ETHYL CORP. - MAGNOLIA
N
WOODS
WOODS
②
③
⑤
④
⑥
⑦
①
A
POND
TANKS
FUEL TANKS
POND
FLARE
HOLDING POND
APPROX. SCALE 1 cm = 110 m

Figure 4.67. Schematic map of Ethyl Corporation, Magnolia - sampling locations for P1 - 9/23/76.

A - EDB and Br_2 facilities

B = EDB facilities

Table 4.46. SAMPLING PROTOCOL FOR ETHYL CORPORATION, MAGNOLIA, ARKANSAS

Period	Cycle	Location	Sample Size	Type of Sample
P1 5/17/77	C1	L1	2 core[a]	SHHC-V
		L1	2 core	SHHC-SV
		L2		VHHC-V/SV[b]
		L3		VHHC-V/SV[d]
		L4	1 ℓ	WHHC-V/SV[c]
		L5	1 ℓ	WHHC-V/SV[e]
		L5		VHHC-V/SV[f]
		L6	2 core	SHHC-V
		L6	2 core	SHHC-SV
		L6	1 ℓ	WHHC-V/SV[e]
		L7	2 core	SHHC-V
		L7	2 core	SHHC-SV

[a] Core ∿5 cm diameter, 13 cm depth.

[b] Needles stripped from 40 cm of pine bough sampled at ∿5 m above ground from trees showing damage.

[c] Wide, slow moving portion of stream.

[d] Blackberries.

[e] Well water.

[f] Peaches.

Key to sample type:
SHHC - soil for halogenated hydrocarbons
WHHC - water for halogenated hydrocarbons
VHHC - vegetation for halogenated hydrocarbons
V - for volatile organic analysis
SV - for semi-volatile organic analysis

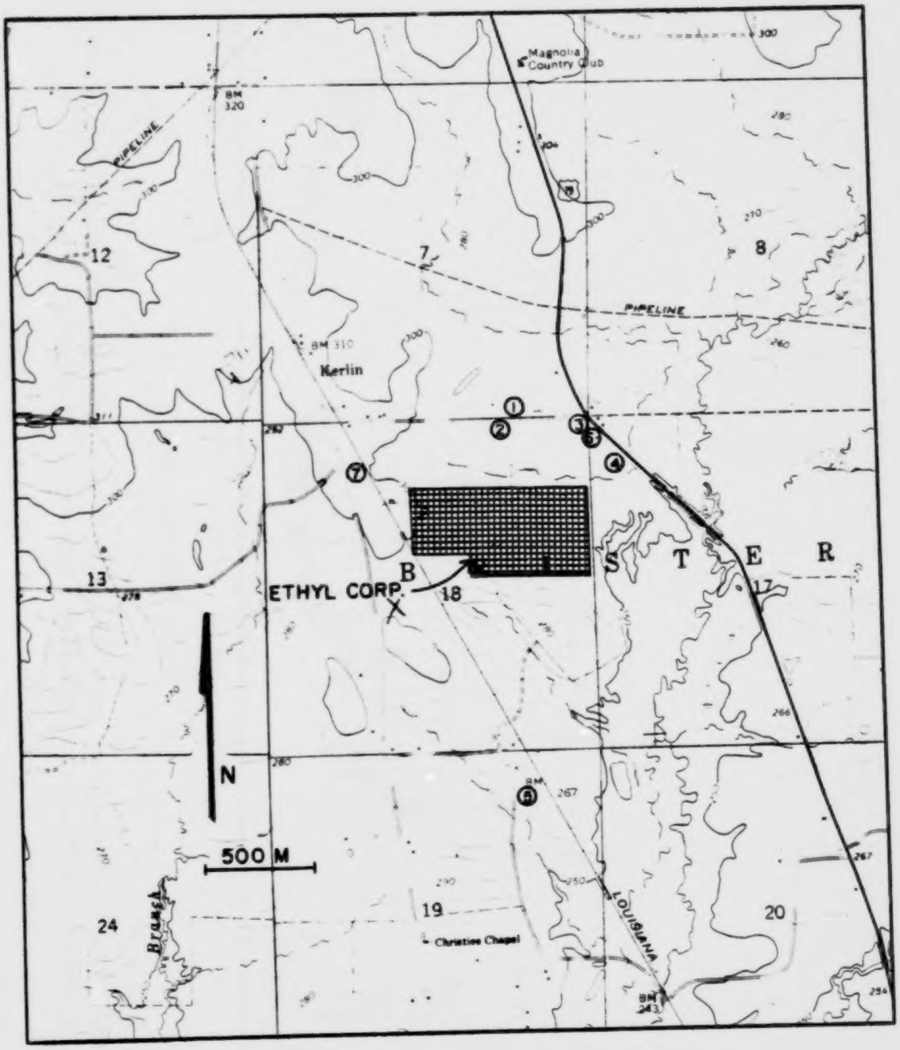

Magnolia Country Club
PIPELINE
BM 320
300
12
7
8
PIPELINE
BM 310
Kerlin
ETHYL CORP.
B
18
S
T
E
R
13
17
N
500 M
19
20
24
Branch
Christies Chapel
LOUISIANA
BM 267
BM 243

Figure 4.68. Map of area in vicinity of Ethyl Corporation, Magnolia, Arkansas - sampling locations for water, soil, sediment, and vegetation for Pl - 5/17/77.

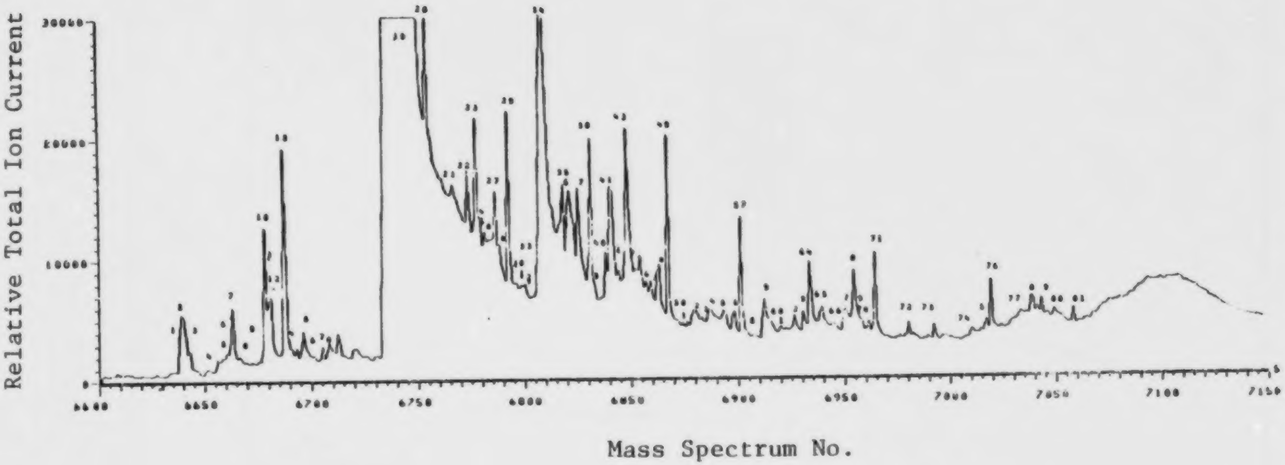


Figure 4.69. Total ion current profile of volatile ambient air pollutants from Ethyl Corp. site, Magnolia, Arkansas (P1/C1/L2).

Table 4.47. CONCENTRATIONS OF HALOGENS AND HALIDES IN AMBIENT AIR SURROUNDING ETHYL CORP.[a,b]

Species	Location L3
Cl_2/Br_2[c]	<70
Br_2[d]	<29
Cl^-/Br^-[c]	<44
Br^-[d]	<14

[a] Samples are from P1/C3.

[b] Values are in $\mu g/m^3$.

[c] By turbidity.

[d] By neutron activation analysis.

and the large concentration probably occurred because a diesel powered tank trailer passed by the sampling location. On the backside of this large peak (Peak No. 20), 1,2-dibromoethane was detected. This is more clearly presented in Figure 4.70 which presents the ion chromatograms for *m/e* 85, *m/e* 109, *m/e* 120 and *m/e* 124. The peaks corresponding to allyl bromide and 1,2-dibromoethane which were identified in this sample are also noted in this figure.

At L3 (see Fig. 4.67) several halogenated organics were detected. The profile for this location is shown in Figure 4.71 and the ion chromatograms are shown in Figure 4.72. In Figure 4.72 the presence of bromopropane, chlorobromoethane, bromodichloromethane and 1,2-dibromoethane are clearly evident. Table 4.48 summarizes the halogenated hydrocarbons identified by GC/MS/COMP in ambient air samples from Ethyl Corp.

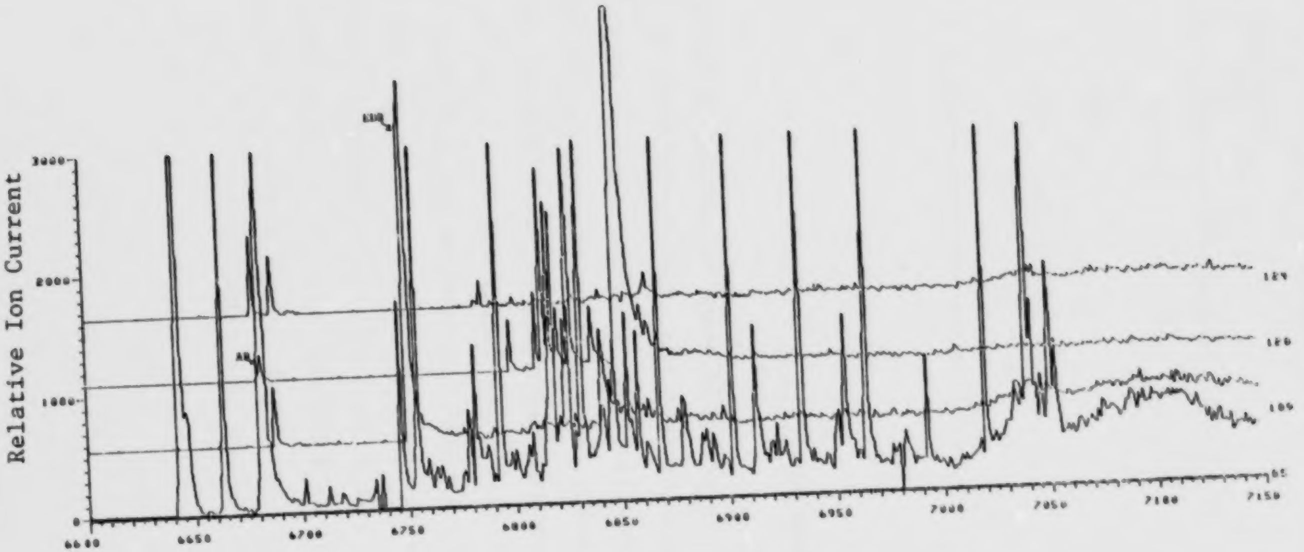


Figure 4.70. Ion chromatograms of ambient air sample from Ethyl Corp. site, Magnolia, Arkansas (P1/C1/L2). AB = alkyl bromide, EDB = ethylene dibromide.

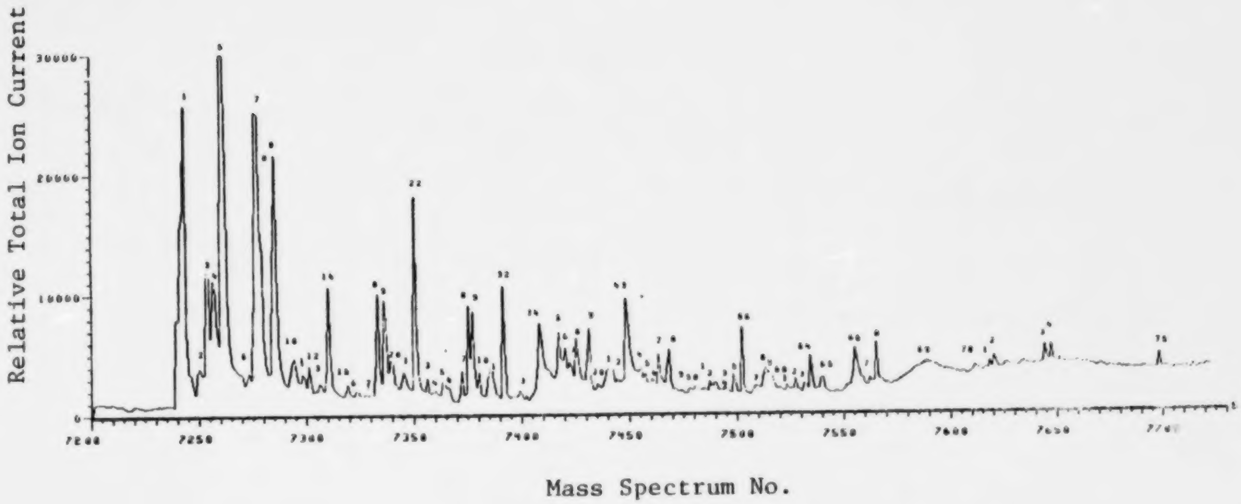


Figure 4.71. Total ion current profile of volatile ambient air pollutants from Ethyl Corp. site, Magnolia, Arkansas (P1/C1/L3).

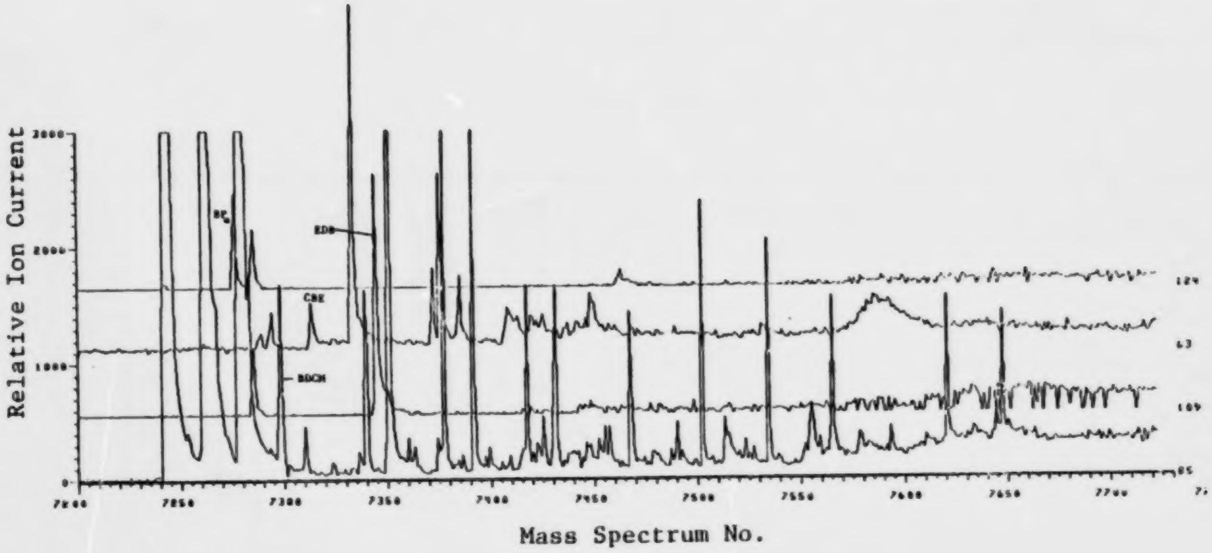


Figure 4.72. Ion chromatograms of ambient air sample from Ethyl Corp. site, Magnolia, Arkansas (P1/C1/L2). BP = bromopropane, CBE = chlorobromoethane, BDCM = bromodichloromethane and EDB = 1,2-dibromoethane.

Table 4.48. HALOGENATED HYDROCARBONS IDENTIFIED BY GC/MS/COMP IN AMBIENT AIR AT ETHYL CORP., MAGNOLIA, ARKANSAS

Compound	Compound
1-chloro-2-bromoethane	1,2-dibromoethane
bromopropane	vinyl bromide
bromodichloromethane	allyl bromide

Quantification of Halogenated Hydrocarbons.--The levels of halogenated hydrocarbons in the ambient air samples surrounding Ethyl Corp. are given in Table 4.49. The highest concentration of any halogenated hydrocarbon of all the samples which were collected at all the sites occurred in the sample taken at L4. The sampling location was approximately 20 yards from the 1,2-dibromoethane synthesis facility. The level of 1,2-dibromoethane was 20,215 ng/m^3.

Estimation of Methyl Chloride, Methyl Bromide, Vinyl Chloride, and Vinyl Bromide.--None of these chemicals were detected by GC/ECD or mass fragmentography.

Ethylene.--The ethylene levels observed are given in Table 4.50. Typical background values were seen.

4.2.4.4 Brominated Organics in Soil, Water and Vegetation

All of the samples described in Table 4.46 were analyzed by the VOA procedure for EDB and other halogenated organics. No EDB was detected in any of the samples nor were any other volatile halogenated organics identified. A soil sample P1/C1/L1 was extracted for semi-volatile organics and submitted to high resolution mass spectral analysis (direct probe) and no halogenated organics were found.

4.2.5 Dow Chemical Co. and Vicinity

During the survey study ambient air monitoring for brominated organics was not conducted at this plant site. However, condensed phase samples were collected and some of these data are presented here.

Table 4.49. HALOGENATED HYDROCARBONS IDENTIFIED AND QUANTIFIED IN AMBIENT AIR SURROUNDING ETHYL CORP., MAGNOLIA, AK

Period/Cycle/Location[a]	Allyl bromide	Bromodichloromethane	1- or 2-Bromopropane	1-Chloro-2-bromo-propane	Ethylene dibromide	Methyl bromide
P1/C1/L1	9.4	-[b]	-	-	227	?
L2	15.8	3.4	16.2	-	174	-
L3	-	6.8	26.6	1.2	21.2	-
P1/C2/L4	-	-	-	-	20,250	T[c]

[a] Refer to Table 4.45 for sampling protocol, values are in ng/m^3

[b] - = not detected

[c] T = trace detected

Table 4.50. ETHYLENE LEVELS IN AMBIENT AIR

Site[a]	Period/Cycle/Location	ppm
EC	P1/C4/L4	0.76 ± 0.06
	P1/C4/L5	0.60 ± 0
	P1/C4/L6	0.70 ± 0.10
	P1/C4/L7	0.73 ± 0.13

[a] See Table 4.45 and Figure 4.67 for protocol and locations.

4.2.5.1 Sampling

Samples of soil, water and vegetation were collected in the vicinity of Dow Chemical Co., Magnolia, AK. The sampling protocol is given in Table 4.51 and Figure 4.73.

4.2.5.2 Brominated Organics in Soil, Water and Vegetation

Environmental samples were analyzed by the VOA procedure for the presence of EDB and other volatile halogenated organics. The results are given in Table 4.52.

Table 4.51. SAMPLING PROTOCOL FOR DOW CHEMICAL CO. MAGNOLIA, ARKANSAS

Period	Cycle	Location	Sample Size	Type of Sample
P1 5/17/77	C1	L1	2 cores[a]	SHHC-V
		L1	2 cores	SHHC-SV
		L1		VHHC-V/SV
		L2	1 ℓ	WHHC-V/SV[b]
		L3	1 ℓ	WHHC-V/SV[c]
		L4	2 cores	SHHC-V
		L4	2 cores	SHHC-SV
		L5	1 ℓ	WHHC-S/SV[d]
		L5		VHHC-S/SV[e]
		L5		VHHC-S/SV[f]
		L6	2 cores	SHHC-S
		L6	2 cores	SHHC-SV
		L7	1 ℓ	WHHC-S/SV[b]

[a] Core ∿5 cm diameter, 13 cm depth.

[b] ∿2 m wide, ∿15 cm deep in dry weather (no rain for 1 week).

[c] Farm ponds.

[d] Lake.

[e] Leaves of pecan tree.

[f] Potatoes.

Key to sample type:
SHHC - soil for halogenated hydrocarbons
WHHC - water for halogenated hydrocarbons
VHHC - vegetation for halogenated hydrocarbons
V - for volatile organic analysis
SV - for semi-volatile organic analysis

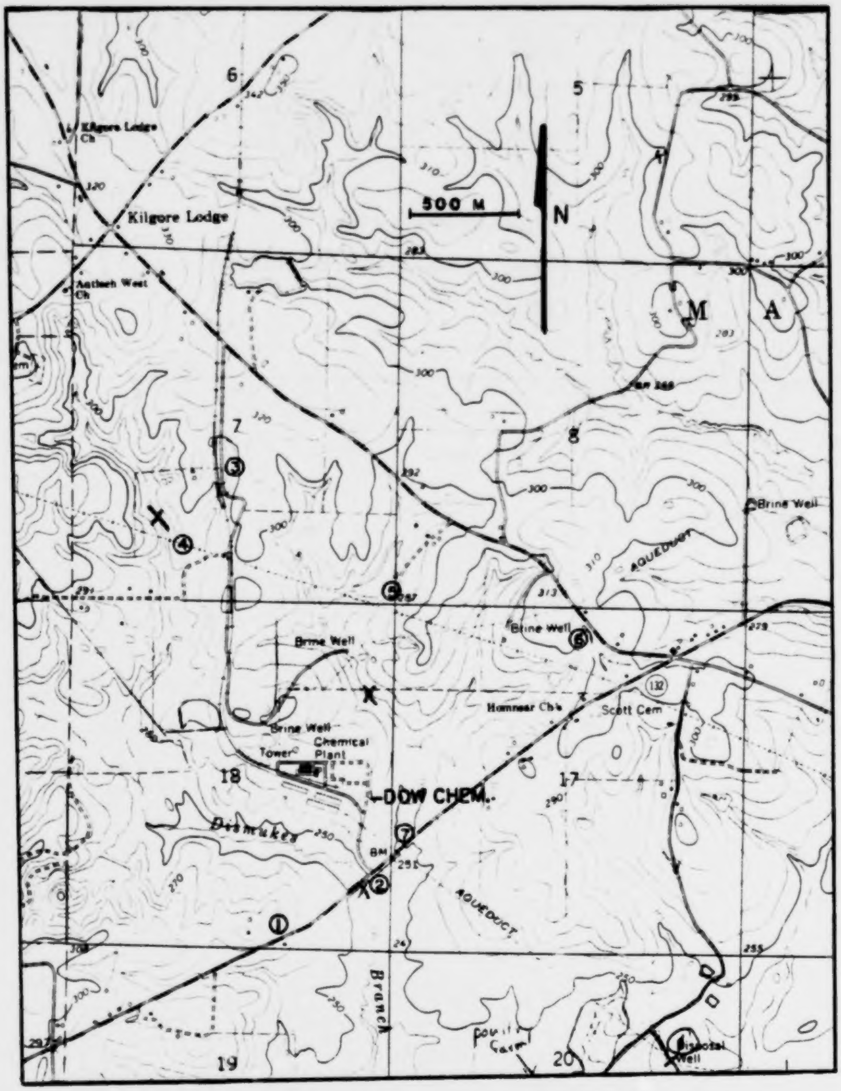

500 M
N
Kilgore Lodge Ch
Kilgore Lodge
Antioch West Ch
6
5
7
8
18
17
19
20
M
A
Brine Well
Brine Well
Brine Well
Brine Well
Chemical Plant
Tower
DOW CHEM.
Hannear Ch
Scott Cem
132
AQUEDUCT
AQUEDUCT
Dismukes
Branch
BM
Disposal Well
①
②
③
④
⑤
⑥
⑦
⑧

Figure 4.73. Map of area in vicinity of Dow Chemical Company, Magnolia, Arkansas - sampling locations for water, soil, sediment and vegetation for P1 - 5/17/77.

Table 4.52. VOA ANALYSIS OF ENVIRONMENTAL SAMPLES FROM THE VICINITY OF DOW CHEMICAL CO., MAGNOLIA, AK

Period/Cycle/Location	Sample Type	EDB
P1/C1/L1	Soil	ND
L2	Water	ND
L3	Water	ND
L4	Soil	Detected
L5	Vegetation (potatoes)	ND
	Vegetation (pecan leaves)	ND
	Water	ND
L6	Soil	ND

5.0 LONG-TERM MONITORING FOR VOLATILE BROMINATED ORGANICS

Sites were selected in the El Dorado and Magnolia areas to continuously monitor for volatile brominated organics in ambient air. The objective was to determine whether significant levels of brominated organics in ambient air were being transported from the bromine industry to populated areas. Thus the specific aim was to assess potential exposure to volatile brominated organics, specifically, 1,2-dibromoethane.

5.1 SAMPLING AND ANALYSIS

Two sites were selected in El Dorado - one on the water tower at Parker's Chapel and the other on a water tower in El Dorado. Figure 5.1 shows the location of these sites with respect to Great Lakes Chemical Corporation and Arkansas Chemical Inc. Three sites were selected in Magnolia and their locations are shown in Figures 5.2-5.4 with respect to the city of Magnolia, Dow Chemical Co. and Ethyl Corporation, respectively.

The sampling and analysis methodology employed in this study is given in Appendix A, Section F.

5.2 RESULTS AND DISCUSSION

The sampling protocols for ambient air samples collected in El Dorado are given in Tables 5.1 and 5.2. 1,2-Dibromoethane was detected on three different days at the Parkers Chapel water tower (Table 5.1). On the first day of sampling, a level of 700 ng/m^3 was measured and the highest value was found during the 26th sampling period at which time it achieved a level of 1,260 ng/m^3. As can be seen in Table 5.1, during these three days of sampling the predominant wind direction was from the general area of the Great Lakes Chemical Corp. Low concentrations of 1-chloro-2-bromoethane, dibromopropane and allyl bromide were found in samples taken on the El Dorado water tower (Table 5.2). In general, these sampling periods represented times when the wind direction was generally from the west to southwest direction.

Tables 5.3-5.5 present the sampling protocols for the air monitoring conducted in Magnolia, AK near Dow Chemical Co. and near Ethyl Corporation,

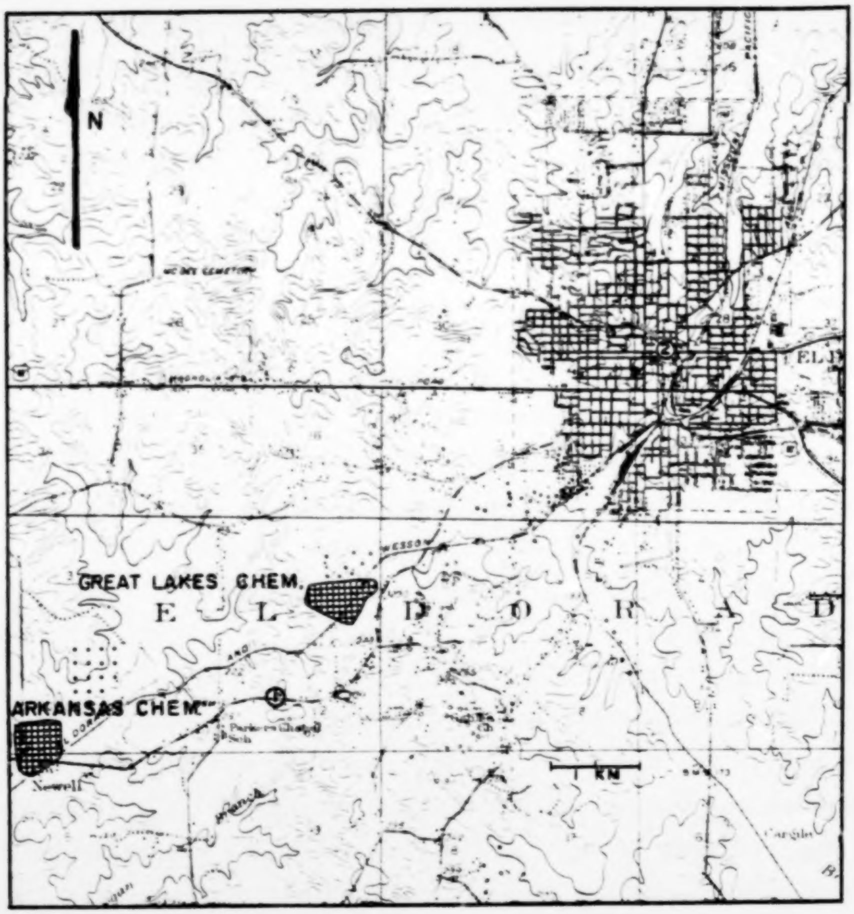

N
GREAT LAKES CHEM.
ARKANSAS CHEM.
E L D O R A D
WESSON
1 KM
Newell
Cargile
①
②

Figure 5.1. Map of El Dorado area - sampling locations for continuous air monitoring.

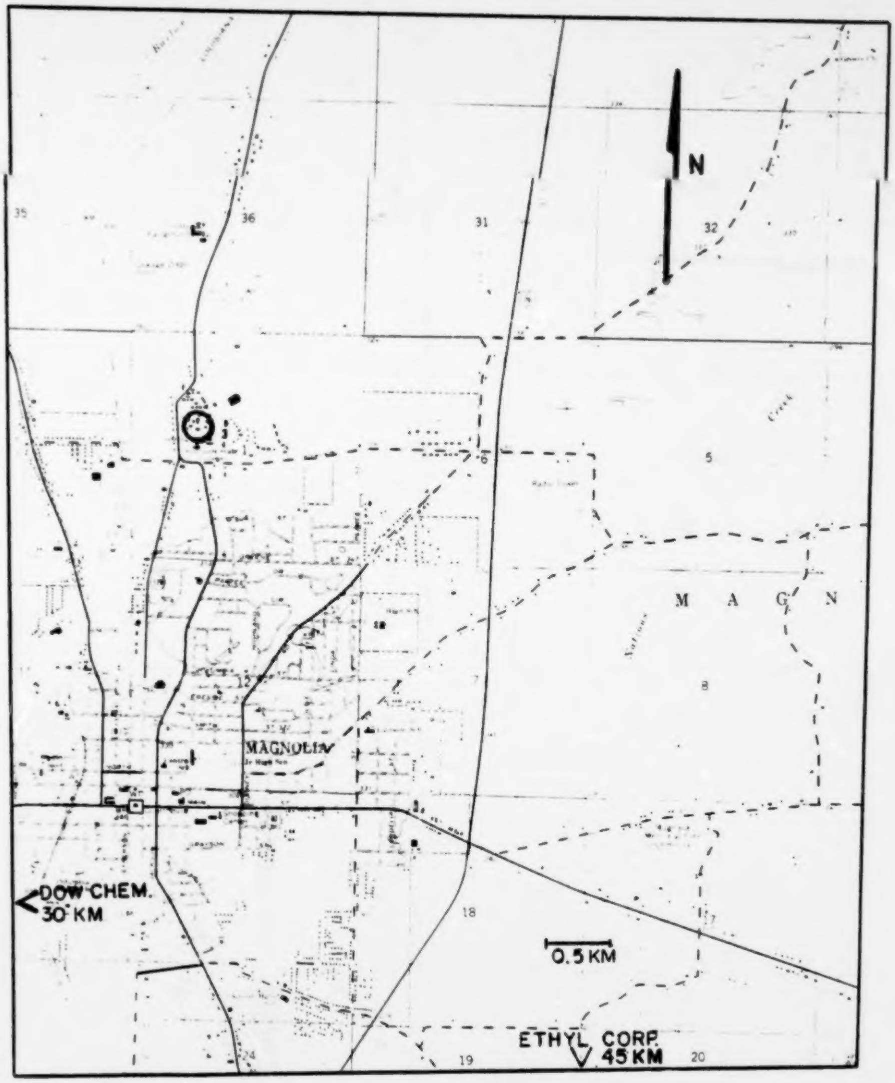
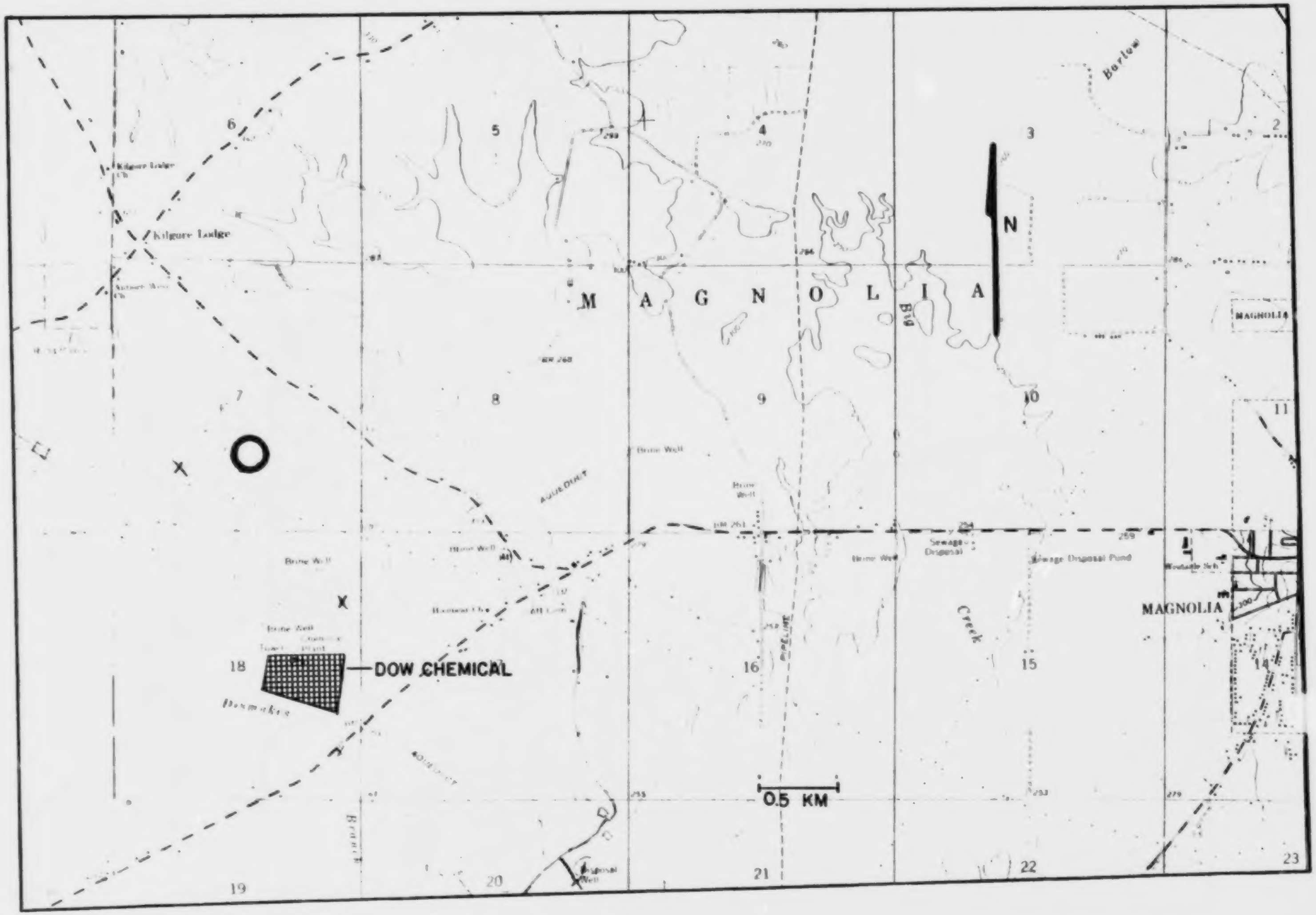

N
35
36
31
32
5
6
M A G N
8
12
MAGNOLIA
DOW CHEM.
30 KM
18
0.5 KM
ETHYL CORP.
45 KM
24
19
20

Figure 5.2. Map of Magnolia area - sampling locations for continuous air monitoring.



Barlow
Kilgore Lodge
M A G N O L I A
N
Big
Creek
MAGNOLIA
Brine Well
Sewage Disposal
Sewage Disposal Pond
AQUEDUCT
DOW CHEMICAL
0.5 KM
Branch
Disposal Well
2
3
4
5
6
7
8
9
10
11
14
15
16
18
19
20
21
22
23

Figure 5.3. Map of area in vicinity of Dow Chemical Company, Magnolia, Arkansas - sampling location for continuous air monitoring.

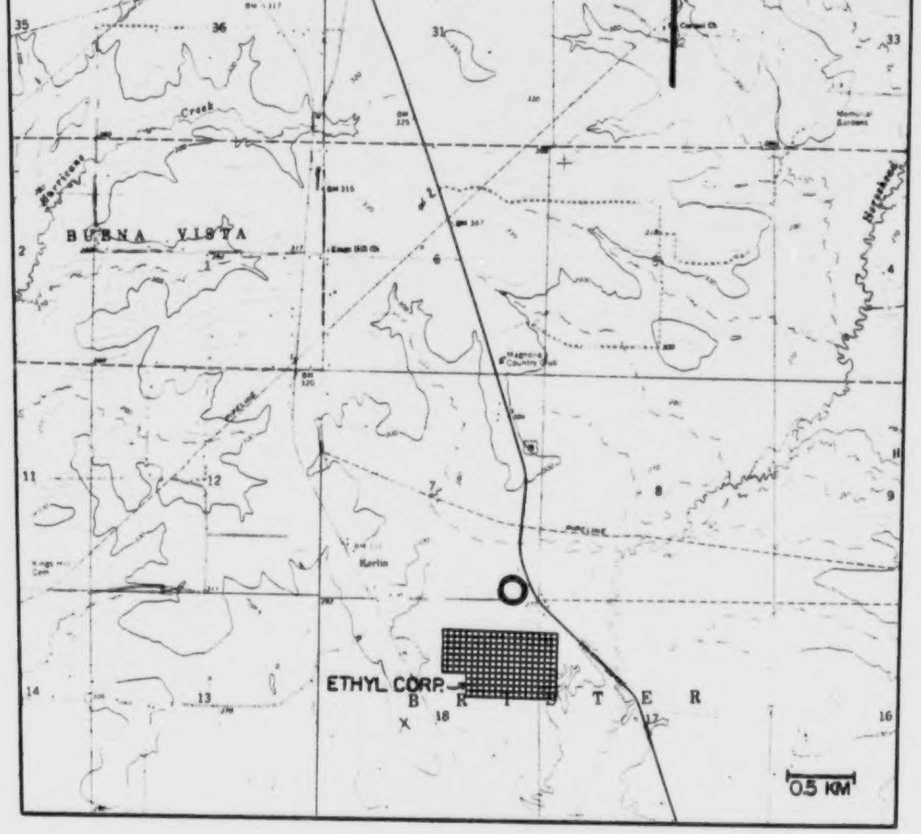

MAGNOLIA
Nations
Walker
BUENA VISTA
Creek
N
ETHYL CORP.
BRISTER
Kerlin
0.5 KM
26
25
30
29
35
36
31
33
2
1
6
5
4
11
12
7
8
9
14
13
18
17
16

Figure 5.4. Map of area in the vicinity of Ethyl Corporation, Magnolia, Arkansas - sampling location for continuous air monitoring.

Table 5.1. SAMPLING PROTOCOL FOR CONTINUOUS AIR MONITORING IN THE EL DORADO, ARKANSAS VICINITY - LOCATION 1: PARKERS CHAPEL WATER TOWER

Period	Volatile Brominated Organics ng/m^3	Time/Date	Volume (m^3)	Meteorology				Comments
				Temp. °C^a	Wind Dir.	Wind speed (Knts)	Precipitation	
P1	700^b	1425, 3/5/77- 1625, 3/6/77	0.131	17/1°	NE-NW	0-10		
P2	ND	1635, 3/6/77- 1706, 3/7/77	0.147	20/-2	NW-SW calm	0-10		
P3	ND	1706, 3/7/77- 1550, 3/8/77	0.136	23/1	calm NW, SW	0-15		
P4	ND	1550, 3/8/77- 1725, 3/9/77	0.153	21/5	calm, SW,S,SE	0-15		
P5	ND	1725, 3/9/77- 1555, 3/10/77	0.134	24/4	SE	5-10		
P6	ND	1555, 3/10/77 1715, 3/12/77	0.152	23/12	SE,W	10-15	2.06 cm	
P7	ND	1715, 3/11/77- 1700, 3/12/77	0.142	23/10	SE,SW,W	5-15		Rain, Wind and water damage to to sampler. Various malodors present.
P8	ND	1700, 3/12/77- 1655, 3/13/77	0.143	27/10	SW,W	5-10		
P9	ND	1655, 3/13/77- 1718, 3/14/77	0.146	29/6	calm S,SW	0-15		Dust storm coming into area.
P10	ND	1718, 3/14/77	0.138	30/17	SW,W	0-10		

(continued)

Table 5.1 (cont'd)

Period	Volatile Brominated Organics ng/m³	Time/Date	Volume (m³)	Meteorology				Comments
				Temp. °C[a]	Wind Dir.	Wind Speed (Knts)	Precipitation	
P11	280[b]	1615, 3/15/77- 1830, 3/17/77	0.158	30/12	N,NE	5-15		
P12	ND	1830, 3/16/77- 1600, 3/17/77	0.129	25/14	NE,E,SE,S	5-10		
P13	ND	1600, 3/17/77- 1708, 3/18/77	0.151	26/16	S,SW,NW	5-15		
P14	ND	1708, 3/18/77 1705, 3/19/77	0.144	21/14	NE,E,SE	0-10		
P15	ND	1705, 3/19/77- 1750, 3/20/77	0.148	20/-1	calm NW,E SE	0-10		
P16	ND	1750, 3/20/77- 1535, 3/21/77	0.130	26/9	calm SE,E,W	0-15		
P17	ND	1535, 3/21/77- 1530, 3/22/77	0.144	26/1	NW,NE	0-10		
P18	ND	1530, 3/22/77- 0900, 3/23/77	0.105	18/1	calm	-		Strong odor, not H_2S.
P19	ND	0900, 3/23/77- 1555, 3/24/22	0.186	23/8	S, Calm	0-5	0.56 cm	
P21	ND	1635, 3/25/77- 1855, 3/26/77	0.158	25/16	SE	5-10		
P22	ND	1855, 3/26/77- 1614, 3/27/77	0.128	25/18	SE,S	5-15	2.67 cm	

(continued)

Table 5.1 (cont'd)

				Meteorology				
Period	Volatile Brominated Organics ng/m^3	Time/Date	Volume (m^3)	Temp. °C[a]	Wind Dir.	Wind Speed (Knts)	Precipitation	Comments
P23	ND	1614, 3/27/77- 1706, 3/28/77	0.149	27/13	S,SE S-SW	-20 G	2.08 cm	
P24	ND	1706, 3/28/77- 1600, 3/29/77	0.144	24/14	S,SW,SE	5-10		
P25	ND	1600, 3/29/77- 1850, 3/30/77	0.161	29/17	calm S,SW,W	5-10		
P26	1,260[b]	1850, 3/30/77- 1353, 3/31/77	0.114	23/17	NW,N,NE	5-10		
P27	ND	1353, 3/31/77- 1200, 4/1/77	0.190	23/11	NE,E	5-10	0.08 cm	
P28	ND	1200, 4/1/77 1515, 4/2/77	0.245	24/15	SE,S,SW	5-10	0.79 cm	
P29	ND	1515, 4/2/77- 1655, 4/3/77	0.205	22/13	calm SW,S,NE	0-15	1.40 cm	
P30	ND	1655, 4/3/77-	0.164	18/15	E,NE, calm W	0-15 (G 22)	0.56 cm	
P31	ND	1752, 4/4/77- 1615, 4/5/77	0.146	18/6	W,NW	0-15 (G 23)		

(continued)

Table 5.1 (cont'd)

Period	Volatile Brominated Organics ng/m^3	Time/Date	Volume (m^3)	Meteorology				Comments
				Temp. °C[a]	Wind Dir.	Wind Speed (Knts)	Precipitation	
P32	ND	1615, 4/5/77- 1825, 4/6/77	0.156	18/4	calm NW,W,SW	0-10		
P33	ND	1825, 4/6/77-	~0.135	29/9	calm W	0-14		

[a] High/low

[b] 1,2-dibromoethane

Table 5.2. SAMPLING PROTOCOL FOR CONTINUOUS AIR MONITORING IN THE EL DORADO, ARKANSAS VICINITY - LOCATION 2: EL DORADO WATER TOWER

				Meteorology				
Period	Volatile Brominated Organics ng/m^3	Time/Date	Volume (m^3)	Temp. °C[a]	Wind Dir.	Wind Speed (Knts)	Precipitation	Comments
P1	2,520[b]	1650, 3/5/77- 1700, 3/6/77	0.145	17/1	NE-NW	0-10		
P2	4,200[b]	1700, 3/6/77- 1840, 3/7/77	0.134	20/-2	NW-SW calm	0-10		
P3	ND	1840, 3/7/77- 1615, 3/8/77	0.129	23/1	calm NW,SW	0-15		
P4	ND	1516, 3/8/77- 1802, 3/9/77	0.170	21/5	calm SW,S,SE	0-15		
P5	560[c]	1802, 3/9/77- 1620, 3/10/77	0.120	24/4	SE	5-10		
P6	ND	1620, 3/10/77- 1746, 3/11/77	0.129	23/12	SE,W	10-15	2.06 cm	
P7	ND	1746, 3/11/77- 1725, 3/12/77	0.142	23/10	SE,SW,W	5-15		
P8	ND	1725, 3/12/77- 1725, 3/13/77	0.144	27/10	SW,W	5-10		
P9	ND	1725, 3/13/77- 1816, 3/14/77	0.149	29/6	calm S,SW	0-15		
P10	ND	1816, 3/14/77- 1645, 3/15/77	0.135	30/17	SW,W	0-10		

(continued)

Table 5.2 (cont'd)

				Meteorology				
Period	Volatile Brominated Organics ng/m^3	Time/Date	Volume (m^3)	Temp. °C^a	Wind Dir.	Wind Speed (Knts)	Precipitation	Comments
P11	ND	1745, 3/15/77- 1855, 3/16/77	0.157	30/12	N,NE	5-15		
P12	700^b	1855, 3/16/77- 1630, 3/17/77	0.129	25/14	NE,E,SE,S	5-10		
P13	ND	1630, 3/17/77- 1745, 3/18/77	0.152	26/16	S,SW,NW	5-15		
P14	ND	1745, 3/19/77- 1730, 3/19/77	0.142	21/14	NE,E,SE	0-10		
P15	ND	1730, 3/19/77- 1810, 3/29/77	0.148	20/-1	calm NW,E, SE	0-10		
P16	ND	1810, 3/20/77- 1600, 3/21/77	0.157	26/9	calm SE,S,W	0-15		
P17	ND	1600, 3/21/77- 1455, 3/22/77	0.183	26/1	NW,NE	0-10		
P18	ND	1455, 3/22/77- 0925, 3/23/77	0.116	18/1	calm	-		
P19	ND	0925, 3/23/77- 1625, 3/24/77	0.203	23/8	S calm	0-5	0.56 cm	
P21	ND	1600, 3/25/77- 1925, 3/26/77	0.164	25/16	SE	5-10		Raining

(continued)

Table 5.2 (cont'd)

Period	Volatile Brominated Organics ng/m^3	Time/Date	Volume (m^3)	Meteorology				Comments
				Temp. °C^a	Wind Dir.	Wind Speed (Knts)	Precipitation	
P22	ND	1925, 3/26/77- 1652, 3/27/77	0.129	25/18	SE,S	5-15	2.67 cm	Raining
P23	280^d	1652, 3/27/77- 1735, 3/28/77	0.148	27/13	S,SE,W-SW	5-20 (G)	2.08 cm	
P24	ND	1735, 3/28/77- 1625, 3/29/77	0.137	24/14	S,SW,SE	5-10		
P25	ND	1625, 3/29/77- 1922, 3/30/77	0.162	29/17	calm, S,SW,W	5-10		
P26	ND	1922, 3/30/77- 1415, 3/31/77	0.113	23/17	NW,N,NE	5-10		
P27	ND	1415, 3/31/77- 1220, 4/1/77	0.132	23/11	NE,E	5-10	0.08 cm	
P28	ND	1220, 4/1/77- 1450, 4/2/77	--	24/15	SE,S,SW	5-10	0.79 cm	Pump stopped during sampling interval
P29	ND	1450, 4/2/77- 1720, 4/3/77	0.136	22/13	calm, SW,S,NE	0-15	1.40 cm	
P30	ND	1720, 4/3/77-	0.180	18/15	E,NE,calm,W	0-15 (G 22)	0.56 cm	
P31	280	1824, 4/4/77- 1740, 4/5/77	0.152	18/6	W,NW	0-15 (G 23)		

(continued)

Table 5.2 (cont'd)

				Meteorology				
Period	Volatile Brominated Organics ng/m^3	Time/Date	Volume (m^3)	Temp. °C[a]	Wind Dir.	Wind Speed (Knts)	Precipitation	Comments
P32	T	1740,4/5/77-	--	18/4	calm,NW,W,SW	0-10		Pump stopped during sampling interval
P33	260	1856, 4/6/77-	∿0.135	29/9	calm W	0-14		

[a] High/low

[b] 1-chloro-2-bromoethane

[c] dibromopropane

[d] allyl bromide

Table 5.3. PROTOCOL FOR CONTINUOUS AIR MONITORING, MAGNOLIA, ARKANSAS

				Meteorology				
Period	Volatile Brominated Organics ng/m^3	Time/Date	Volume (m^3)	Temp. °C[a]	Wind Dir.	Wind Speed (Knts)	Precipitation	Comments
P1	ND	1740, 4/9/77- 1900, 4/11/77	0.148	29/10	calm S,SW,SE	0-10		
P2	ND	1900, 4/11/77- 1150, 4/13/77	0.123	29/11	calm S,SE	0-10 (G 16)		
P3	ND	1150, 4/13/77- 1605, 4/15/77	0.157	29/11	calm SE	0-10 (G 19)		
P4	T[b]	1605, 4/15/77- 1705, 4/17/77	0.147	29/14	calm SE	0-15		
P5	ND	1705, 4/17/77- 1700, 4/19/77	0.144	28/14	SE,S	5-10	4.98 cm	
P6	ND	1700, 4/19/77- 1750, 4/21/77	0.146	28/18	calm SE	0-10	0.30 cm	
P7	ND	1750, 4/21/77- 2025, 4/23/77	0.152	26/11	E,SE,SW,W calm	0-10	1.37 cm	
P8	T[c]	2025, 2/23/77- 1130, 4/25/77	0.116	26/9	N,NW calm	0-10	trace	
P9	T[b]	1130, 4/25/77- 1450, 4/28/77	0.137	29/7	calm, NW S,SW	0-15		
P10	ND	1450, 4/28/77- 1700, 5/1/77	0.150	28/11	-	0-8		
P11	ND	1700, 5/1/77- 2220, 5/8/77	0.488	29/10	-	0-10		

[a] High/low

[b] dibromochloropropane

[c] allyl bromide

Table 5.4. PROTOCOL FOR CONTINUOUS AIR MONITORING NEAR DOW CHEMICAL COMPANY, MAGNOLIA, ARKANSAS

				Meteorology				
Period	Volatile Brominated Organics ng/m^3	Time/Date	Volume (m^3)	Temp. °C^a	Wind Dir.	Wind Speed (Knts)	Precipitation	Comments
P1	ND	1315, 4/9/77- 1825, 4/11/77	0.012	29/10	calm,S,SW,SE	0-10		
P2	ND	1825, 4/11/77- 1120, 4/13/77	0.123	29/11	calm,S,SW	0-10 (G 16)		
P3	T^b	1120, 4/13/77- 1935, 4/15/77	0.078	29/11	calm, SE	0-10 (G 19)		Sharp odor in air 4/15/77
P4	ND	1935, 4/15/77- 1540, 4/17/77	0.127	29/14	calm, SE	0-15		Flare at Dow emitting grey smoke which was drifting northeast of sampler. Wind from southeast.
P5	ND	1540, 4/17/77- 1620, 4/19/77	0.146	28/14	SE,S	5-10		
P6	ND	1620, 4/19/77- 1925, 4/2/77	<0.153^a	28/18	calm, SE	0-10	4.98 cm	
P7	ND	1925, 4/2/77- 1905, 4/23/77	0.145	26/11	E,SE,SW,W calm	0-10	0.30 cm	Plume seen over plant site with very weak wind blowing in direction of sampler.
P8	ND	1905, 4/23/77- 1100, 4/25/77	0.120	26/9	N,NW,calm	0-10	1.37 cm	
P9	142,^{c} 21^d	1130, 4/25/77- 2010, 4/28/77	0.209	29/7	calm,NW,S,SW	0-15	trace	

(continued)

Table 5.4 (cont'd)

Period	Volatile Brominated Organics ng/m^3	Time/Date	Volume (m^3)	Meteorology				Comments
				Temp. °C[a]	Wind Dir.	Wind Speed (Knts)	Precipitation	
P10	81,[c] 24[d]	2010, 4/28/77- 1740, 4/30/77	0.167	29/13	calm,SW,SE	0-10		Odor in air. wind from plant direction.
P11	ND	1740, 4/30/77- 1130, 5/2/77	0.097	29/12	-	0-8		Faint odor from plant, winds from plant direction.
P12	35,[c] 18[d]	1130, 5/2/77- 1200, 5/4/77	0.146	29/11	-	0-10		

[a] High/low

[b] allyl bromide

[c] 1,2-dibromoethane

[d] dibromochloropropane

Table 5.5. PROTOCOL FOR CONTINUOUS AIR MONITORING NEAR ETHYL CORPORATION, MAGNOLIA, ARKANSAS

Period	Volatile Brominated Organics ng/m^3	Time/Date	Volume (m^3)	Meteorology				
				Temp. °C[a]	Wind Dir.	Wind Speed (Knts)	Precipitation	Comments
P1	ND	1130, 4/9/77 1130, 4/11/77	<0.144[a]	29/10	calm, S,SW,SE	0-10		
P2	ND	1800, 4/11/77- 1050, 4/13/77	0.122	29/11	calm S,SE	0-10 (G 16)		
P3	ND	1050, 4/13/77- 1900, 4/15/77	0.202	29/11	calm SE	0-10 (G 19)		
P4	ND	1900, 4/15/77- 1425, 4/17/77	0.130	29/14	calm SE	0-15		
P5	ND	1435, 4/17/77 1535, 4/19/77	0.147	28/14	SE,S	5-10		
P6	ND	1535, 4/19/77- 1845, 4/21/77	0.134	28/18	calm, SE	0-10	4.98 cm	Odor of bromine.
P7	ND	1845, 4/21/77- 1750, 4/23/77	0.141	26/11	E,SE,SW,W	0-10	0.3 cm	
P8	ND	1750, 4/23/77- 1100, 4/23/77	0.123	26/9	N,NW,calm	0-10	1.37 cm	
P9	ND	1100, 4/25/77- 1905, 4/28/77	<0.120[a]	29/7	calm, NW SW,S	0-15	trace	
P10	57[b]	1905, 4/28/77- 1625, 4/30/77	0.130	29/13	calm,SW	0-10		

[a] High/low

[b] 1,2-dibromoethane

respectively. In a few of the ambient air samples taken from these sites, dibromochloropropane (DBCP), allyl bromide and 1,2-dibromoethane were detected. Traces of DBCP and allyl bromide were detected at the air montoring station on the Southern Arkansas University campus. 1,2-Dibromoethane and DBCP were detected in ambient air samples taken at a sampling station located north of Dow Chemical Co. (Table 5.4). During the periods in which the brominated organics were detected, the wind direction was generally from the southeast, and south to southwest directions (Table 5.4). During one sampling period, a low concentration of 1,2-dibromoethane was detected in an ambient air sample taken north of Ethyl Corporation (Table 5.5).

6.0 CHARACTERIZATION OF ENVIRONMENTAL MEDIA ASSOCIATED WITH BROMINE INDUSTRY

6.1 TECHNICAL STRATEGY

6.1.1 Sampling

As pointed out in Section 4.1, the strategy of the Survey Study was to evaluate the analytical techniques employed for characterizing ambient air and to acquire a maximum amount of information about the chemicals surrounding the bromine industry. With this information in hand as well as the information which was acquired during the long-term continuous monitoring for volatile organic vapors and from condensed phase media for semi-volatile and volatile brominated organics, we proceeded to design a sampling and analysis regime to more extensively study the environmental media surrounding the bromine industry. The concept included extensive sampling of air, water, soil, sediment and biota on the plant sites as well as off-site. Subsequent prioritization of the samples for analysis was necessary in order to best characterize the potential contamination of environmental media by the activities associated with the bromine industry in El Dorado and Magnolia, AK. The sampling strategy included collection of samples immediate and distant from the various industrial sites in order to possibly demonstrate the transport of brominated organics. The sampling strategy was designed not only to investigate transport of brominated organics but also the potential impact on populated areas.

The sampling methods employed during this phase of the program were as described in Appendix A which provides the analytical protocols.

6.1.2 Prioritization of Sample Analysis

Table 6.1 presents the inventory of samples which were collected in Southern Arkansas between July 15 and August 5, 1977. As indicated in the table, a total of 439 samples was collected. However, samples were selected for analysis based upon several criteria which were used to provide a guideline in prioritizing these samples for analysis. The samples of ambient air were selected on the basis of the most favorable meteorological

Table 6.1. INVENTORY OF SAMPLES COLLECTED IN SOUTHERN ARKANSAS (7/15/77 to 8/5/77)[a]

Type of Sample	Great Lakes, El Dorado	Velsicol[b] El Dorado	Ethyl Corp. Magnolia	Dow Chemical Magnolia	Great Lakes Marysville	Other	Arkansas Chemical Co. - El Dorado	Total
Tenax GC/Carbon (air)[c]	21	19	15	13	1	1	0	70
Impingers (halides, air)[c]	16	16	12	16	4	0	0	64
Hi-Vol Filters (air)	4	4	6	6	2	0	8	30
Vacuum Can. (air)[c]	18	15	14	6	4	0	0	57
Soil	20	19	20	20	0	8	0	87
Water	25	5	3	11	0	0	0	44
Vegetation	23	5	5	4	0	0	0	37
Sediment	14	5	2	4	0	0	0	25
Milk	3	1	1	0	0	0	0	5
Miscellaneous	9	2	1	0	0	8	0	20
								439

[a] Samples indicated for an industrial site include both on property and vicinity samples.

[b] Formerly Michigan Chemical Co.

[c] Each sampling train counted as a sample even though two analyses were made.

conditions with respect to the sampling locations and the proximity of the industrial facility. Other environmental media such as soil, water, sediment and biota were selected for analysis in the initial phases of the program based upon samples taken in the immediate vicinity of the plant area but off-site. When environmental samples collected off-site indicated the presence of brominated compounds, then additional samples more distant from the plant sites were selected for analysis.

6.1.3 Ozone Measurements in El Dorado, AK

During the period from July 22-August 12, hourly ozone concentrations were tabulated. Appendix A, Section M describes the techniques used for determining the ozone concentration. The results are given in Appendix D.

6.2 RESULTS AND DISCUSSION

6.2.1 Great Lakes Chemical Corporation and Vicinity

6.2.1.1 Sampling

The sampling protocols for ambient air, water, soil, etc. surrounding Great Lakes Chemical Corporation in El Dorado, AK are given in Tables 6.2-6.4. The sampling period, cycle, location, sampling time, volume and type of sample as well as meteorological conditions are described; the corresponding locations are shown on Figures 6.1-6.5.

6.2.1.2 Inorganics in Ambient Air

The halides and halogens which were quantitated in ambient air surrounding Great Lakes Chemical Co. are given in Table 6.5. The turbidimetric method was used for determining halide and halogen. The values given in Table 6.5 are expressed as chloride and molecular chlorine. However, if bromide or bromine was the predominant species, the values would be multiplied by 1.5. The highest concentration of halide was observed at location 2 at which time it reached a level of 274 $\mu g/m^3$. For this period L4 represents the upwind sample.

6.2.1.3 Brominated and Other Organics

Air.--Table 6.6 presents the ambient air levels of volatile brominated organics which were detected during the five day period. The highest concentration was 271,283 ng/m^3 of 1,2-dibromoethane which occurred at location 2 during the second sampling period. This represented a downwind sampling station approximately 200 yds from the organic synthesis facility.

Table 6.2. SAMPLING PROTOCOL FOR AMBIENT AIR SURROUNDING GREAT LAKES CHEMICAL CORP.,

Period	Cycle	Location	Sampling Time	Sampling Volume (ℓ)	Type of Sample	T(°C)	Meteorological Conditions		
							%RH	Wind Direction Speed (kmph)	Other
P1 7/17/77	C1	L0	1955-1420 (7/18/77)	100	HHC^{ab}				
P2 7/18/77	C1	L1	1139-1240 (7/19/77)	202	HHC^{ab}				
		L2	1155-1305 (7/19/77)	204	HHC^{ab}				
		L3	1242-1315 (7/19/77)	199	HHC^{ab}				
		L4	1543-1352 (7/19/77)	129	HHC^{ab}				
		L5	1514-1334 (7/19/77)	208	HHC^{ab}	20-35		E,SE, calm, N	
		L1	1438-1800	246	CBD,CBN^{c}				
		L2	1444-1807	238	CBD,CBN^{c}				
		L3	1244-1815	356	CBD,CBN^{c}				
		L4	1359-1824	265	CBD,CBN^{c}				
		L5	1530-1335 (7/19/77)	1,949,000	Hi-Vol^{b}				
P3 7/19/77	C1	L1	1256-1110 (7/20/77)	192	HHC^{ab}				
		L2	1310-1121 (7/20/77	180	HHC^{ab}				
		L3	1321-1131 (7/20/77)	188	HHC^{ab}				Strong odor of H_2S
		L4	1400-1147 (7/20/77)	123	HHC^{ab}				
		L5	1347-1139 (7/20/77)	185	HHC^{ab}	20-32	90	N, NE, calm NE to W/3-7	
		L1	1250-1725	204	CBD,CBN^{c}				
		L2	1310-1735	247	CBD,CBN^{c}				
		L3	1317-1738	266	CBD,CBN^{c}			N, calm	Strong odor of H_2S
		L4	1355-1747	254	CBD,CBN^{c}				
		L6	1855	0.5	VAC				
		L7	1858	0.5	VAC				
		L5	1345-1455 (7/20/77)	2,051,000	Hi-Vol^{b}				
P4 7/20/77)	C1	L1	1118-1032 (7/21/77)	188	HHC^{ab}	20-27	60-90	S,with periods of calm 3-6	Upset 1730
		L2	1127-1047 (7/21/77)	<189	HHC^{ab}				Pump stopped during interval
		L3	1137-1130 (7/21/77)	193	HHC^{ab}				Upset 1730
		L4	1152-1150 (7/21/77)	129	HHC^{ab}				Raining 1150
		L5	1147-1143 (7/21/77)	194	HHC^{ab}				
		L1	1018-1520	220	CBD,CBN^{c}			gusty unstable pattern	
		L2	1024-1527	216	CBD,CBN^{c}				
		L3	1031-1533	247	CBD,CBN^{c}				
		L4	1058-1540	279	CBD,CBN^{c}				

(continued)

Table 6.2 (cont'd)

							Meteorological Conditions		
Period	Cycle	Location	Sampling Time	Sampling Volume (ℓ)	Type of Sample	T(°C)	%RH	Wind Direction Speed (kmph)	Other
P4 7/20/77	C1	(Continued)							
		L1	1520	0.5	VAC				
		L2	1530	0.5	VAC				
		L3	1533	0.5	VAC				
		L4	1540	0.5	VAC				
		L5	1512	0.5	VAC				
		L8	1730	0.5	VAC				Middle of Methylchloride storage tanks
		L9	1732	0.5	VAC				Upwind of Methylchloride storage tanks
		L5	1500-1520 (7/21/77)	1,928,000	Hi-Vol[b]				
P5 7/21/77	C1	L1	1042-0845 (7/22/77)	179	HHC[ab]	20-30	60-90	S,NW-NE,calm/1-8	
		L2	1115-0900 (7/22/77)	176	HHC[ab]				
		L3	1138-0910 (7/22/77)	174	HHC[ab]				
		L4	1210-0950 (7/22/77)	117	HHC[ab]				
		L5	1[illegible]0-0925 (7/22/77)	175	HHC[ab]				
		L1	1010-1455	205	CBD,CBN[c]			S,SW/5-6	
		L2	1016-1500	216	CBD,CBN[c]				
		L3	1025-1504	249	CBD,CBN[c]				Bromine upset at N1045
		L4	1031-1507	221	CBD,CBN[c]				
		L1	1230	0.5	VAC				Near cooling water tower
		L2	1230	0.5	VAC				
		L3	1230	0.5	VAC				
		L4	1212	0.5	VAC				
		L1	0845 (7/22/77)	0.5	VAC				
		L2	0900 (7/22/77)	0.5	VAC				
		L3	0910 (7/22/77)	0.5	VAC				
		L4	0950 (7/22/77)	0.5	VAC				
		L5	0925 (7/22/77)	0.5	VAC				
		L5	1525-0931 (7/22/77)	1,475,000	Hi-Vol[b]				

[a] DuPont sampler 3-6 ft elevation.

[b] Overnight sampling.

[c] Nutech Model 220 sampler 3-6 ft elevation.

Locations shown in Figures 6.1 and 6.2

Key to Sample Type:

HHC - Halogenated Hydrocarbon
CBN - Bromine and Chlorine
CBD - Bromide and Chloride
VAC - Aluminum Vacuum Can

Table 6.3. SOIL SAMPLING PROTOCOLS SURROUNDING AND ON GREAT LAKES CHEMICAL CORP., EL DORADO, ARKANSAS

Period	Cycle	Location	Sample Type	Sample Size	Comments
P1	C1	L1[a]	S/HHC	2 cores	Taken $\sim$6 M from the road in school yard
7/17/77		L2[a]	S/HHC	2 cores	Parkers Chapel School
		L3[a]	S/HHC	2 cores	Samples from dry ditch beside railroad
P4	C1	L4[a]	S/HHC	2 cores	
7/20/77		L5[a]	S/HHC	2 cores	
		L6[a]	S/HHC	2 cores	West of methyl bromide storage in a swampy area
		L7[a]	S/HHC	2 cores	
P5	C1	L8[b]	S/HHC	2 cores	
7/21/77		L9[b]	S/HHC	2 cores	Northeast $\sim$30 M from laboratory building
		L10[b]	S/HHC	2 cores	On road to south dump
		L11[b]	S/HHC	2 cores	$\sim$20 M west of holding pond on south edge of property
		L12[b]	S/HHC	2 cores	
		L13[a]	S/HHC	2 cores	
		L14[a]	S/HHC	2 cores	
		L15[a]	S/HHC	2 cores	
		L16[a]	S/HHC	2 cores	
P7	C1	L17[a]	S/HHC	2 cores	
7/23/77					
P8	C1	L18[a]	S/HHC	2 cores	
7/24/77		L19[a]	S/HHC	2 cores	

[a] See Figure 6.3 for map of sample locations.

[b] See Figure 6.4 for map of sample locations.

S = soil samples
HHC = for halogenated hydrocarbon analysis.

Table 6.4. WATER AND SEDIMENT SAMPLING PROTOCOL SURROUNDING AND ON GREAT LAKES CHEMICAL CORPORATION AND THE EL DORADO, ARKANSAS AREA

Period	Cycle	Location	Sample Type	Sample Size (ℓ)	Comments
P1 7/17/77	C1	L1	SD/HHC	2	In swampy area
		L2	SD/HHC	2	
			W/HHC	2	
P3 7/19/77	C1	L3	W/HHC	2	Roof run off during rain
		L4	W/HHC	2	
P4 7/20/77	C1	L5	W/HHC	2	Hard bottom ∿ 21 M east (downstream) of culvert under road - directly draining from Great Lakes
			SD/HHC	2	
		L6	SD/HHC	2	Puddle east side of Lion oil tank
			W/HHC	2	
		L7	W/HHC	2	Pond ∿ 60 M in diameter with oil slick
		L8	W/HHC	2	Clear running water
			SD/HHC	2	
		L9	W/HHC	2	Creek
			SD/HHC	2	
P5 7/21/77	C1	L10	W/HHC	2	Out fall of Great Lakes [a]
			SD/HHC	2	
		L11	W/HHC	2	Upstream of out fall[a]
			SD/HHC	2	
		L12	W/HHC	2	Hard clay (grey)
			SD/HHC	2	
		L13	W/HHC	2	Water backed up in reclaimation area
			SD/HHC	2	Clay/sand bottom, probably new since the entire area was recently graded.
		L14	SD/HHC	2	Pond 200 M north of Parker's Chapel water tower
			W/HHC	2	
P7 7/23/77	C1	L15	W/HHC	4	Creek
			SD/HHC	4	
P8 7/24/77	C1	L16	W/HHC	2	Stream
			SD/HHC	2	
		L17	W/HHC	2	Well water (9 M deep)
		L18	W/HHC	2	Pond
			SD/HHC	2	
		L19	W/HHC	2	Well water
P13 7/29/77	C1	L10	W/HHC	2	Out fall of Great Lakes
		L11	W/HHC	2	Upstream of out fall

[a] Identified by Jarrell Southall, Arkansas State Pollution Control and Ecology.

Locations are shown in Figure 6.5.

W = Water sample
SD = Sediment sample
HHC = for halogenated hydrocarbon analysis

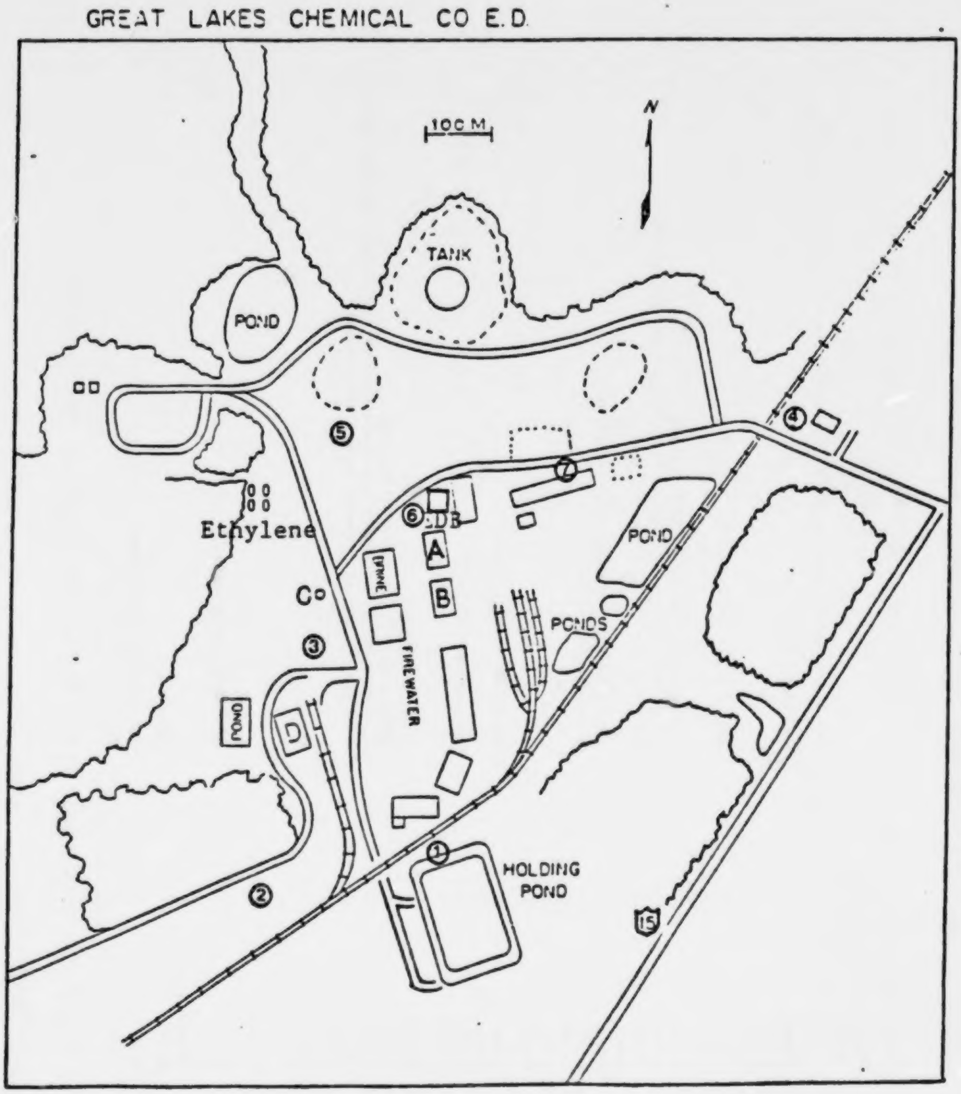

GREAT LAKES CHEMICAL CO E.D.
100 M
N
TANK
POND
⑤
⑦
⑥
EDB
A
B
Ethylene
Co
FIREWATER
POND
PONDS
③
POND
D
①
HOLDING POND
②
15
④

Figure 6.1. Schematic map of Great Lakes Chemical Company, El Dorado, AK - Air sampling locations for P2 (7/18/77) through P5 (7/21/77).

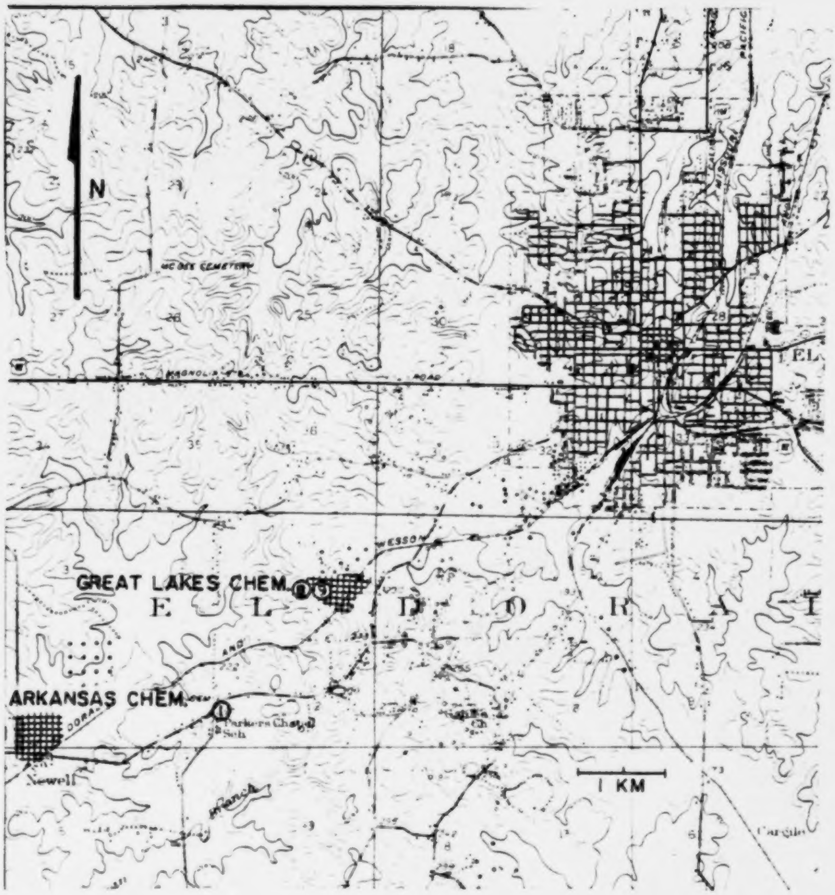

N
GREAT LAKES CHEM.
ARKANSAS CHEM.
E L D O R A
1 KM
Newell
WESSON

Figure 6.2. Map of Great Lakes Chemical Co. Vicinity, El Dorado, Arkansas - air sampling locations (7/17/77 - 7/24/77).

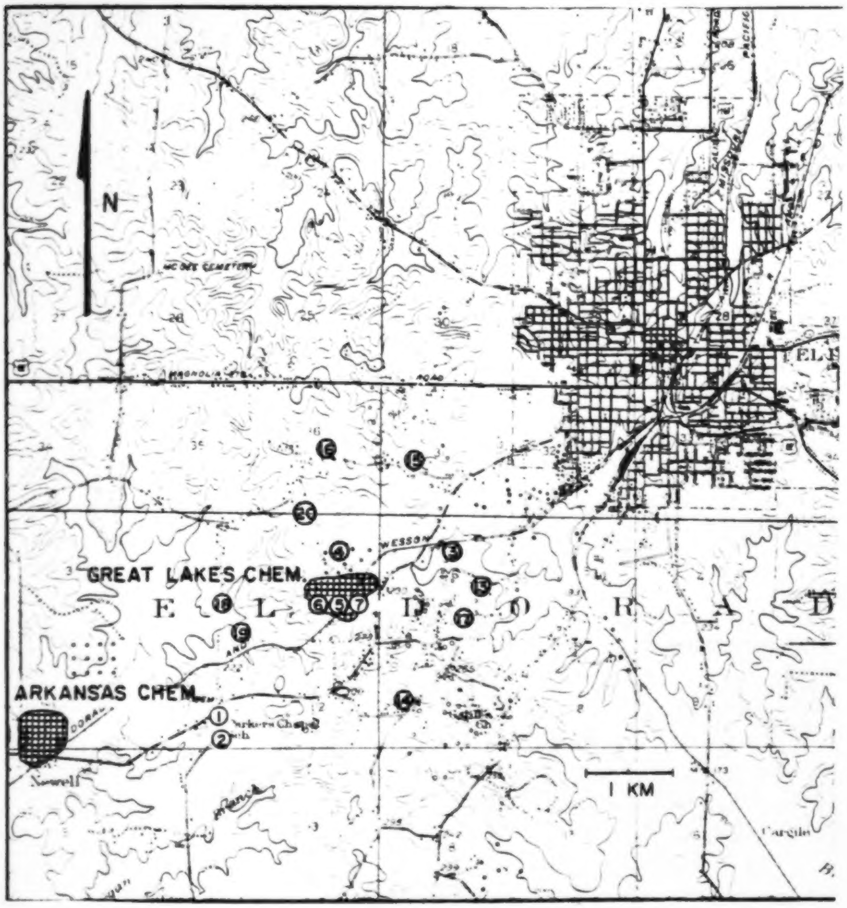

N
GREAT LAKES CHEM.
ARKANSAS CHEM.
E L D O R A D
WESSON
MAGNOLIA ROAD
1
2
4
6
5
7
1 KM

Figure 6.3. Map of Great Lakes Chemical Co. Vicinity, El Dorado, Arkansas - soil sampling locations (7/17/77 - 7/20/77).

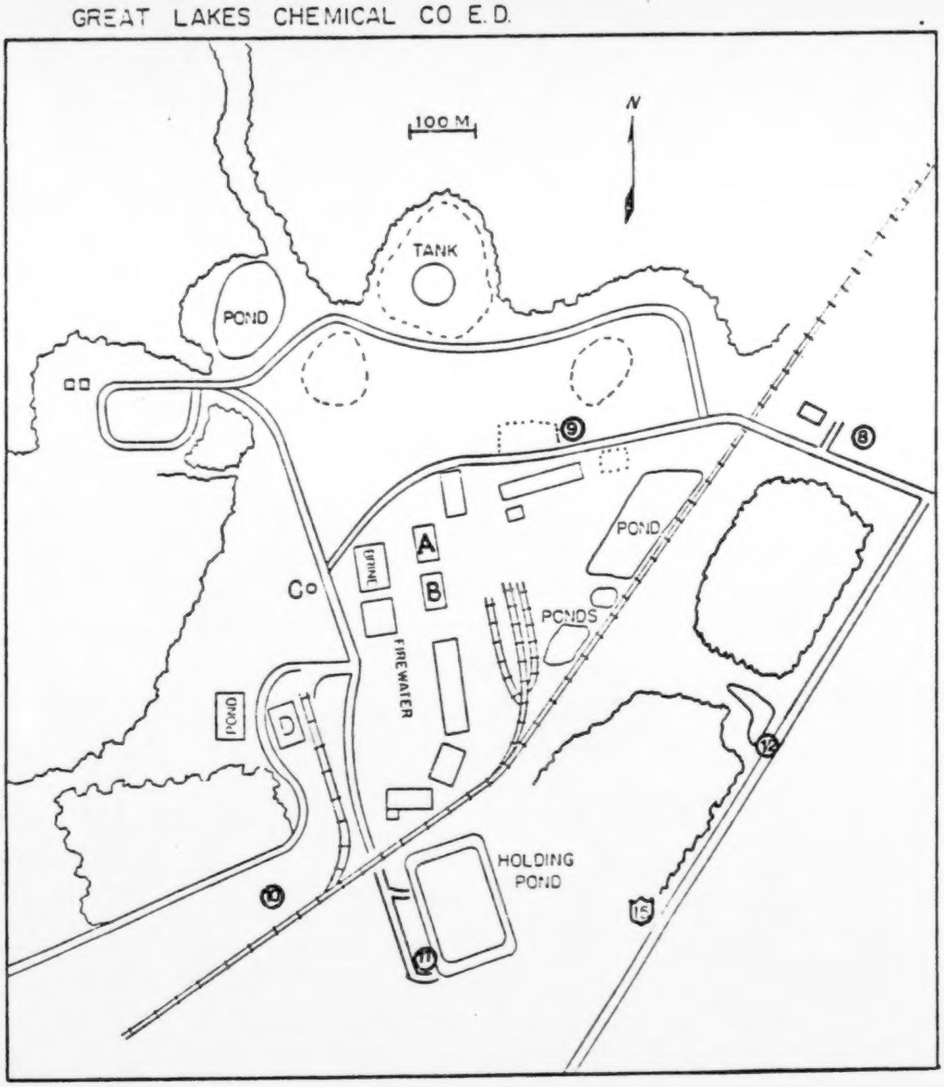

GREAT LAKES CHEMICAL CO E.D.
100 M
N
TANK
POND
Co
BRINE
A
B
FIREWATER
POND
D
POND
PONDS
HOLDING POND
9
8
10
11
12
15

Figure 6.4. Schematic map of Great Lakes Chemical Company, El Dorado, Arkansas -- Soil Sampling Locations. (7/21/77)

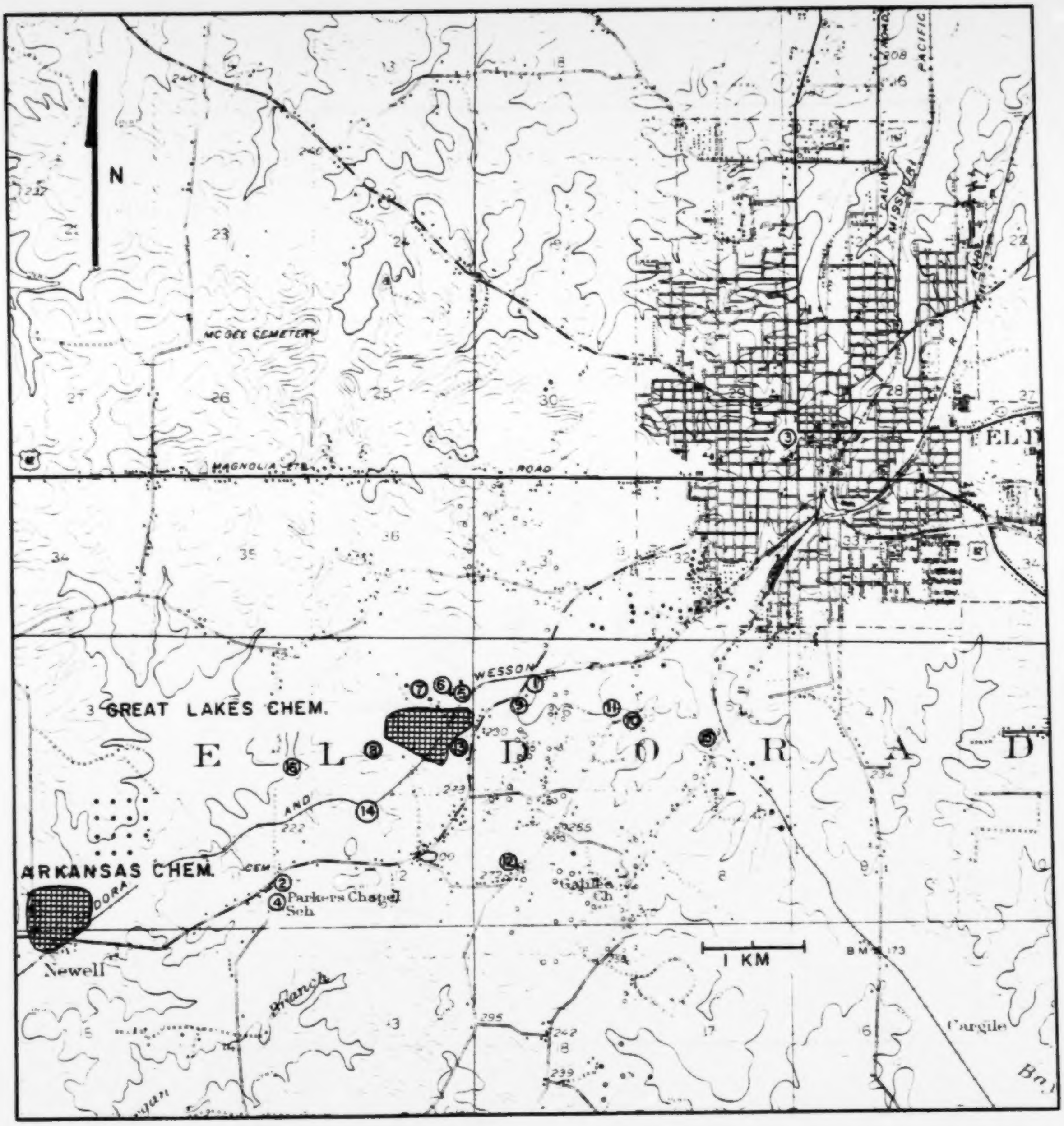

N
MC GEE CEMETERY
MAGNOLIA
ROAD
MISSOURI
PACIFIC
WESSON
GREAT LAKES CHEM.
ARKANSAS CHEM.
E L D O R A D O
ELD
Parkers Chapel Sch
Newell
Branch
Cargile
1 KM
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16

Figure 6.5. Vicinity map of Great Lakes Chemical Company, El Dorado, Arkansas - Water and sediment sampling locations (7/17/77 - 7/24/77).

Table 6.5. HALIDES AND HALOGENS QUANTITATED IN AMBIENT AIR SURROUNDING GREAT LAKES CHEMICAL CORP., EL DORADO, AK

Period/Cycle/Location[a]	Halide as Cl^{-}[b] $\mu g/m^3$	Halogen as Cl_2[b] $\mu g/m^3$
P2/C1/ L1	244 ± 120	58 ± 9
L2	274 ± 184	217 ± 16
L4	< 9	34 ± 8
P3/C1/ L1	151 ± 34	49 ± 2
L2	26 ± 13	63 ± 2
L3	13 ± 8	71 ± 21
P5/C1/ L1	54 ± 16	88 ± 15
L3	113 ± 53	56 ± 9

---

[a] Refer to Table for sampling protocol

[b] Values are expressed as Cl^- or Cl_2, however if Br^- or Br_2 is the predominate species, the values should be multiplied by 1.5.

Table 6.6. AMBIENT AIR LEVELS OF VOLATILE BROMINATED ORGANICS SURROUNDING GREAT LAKES CORP., EL DORADO, AK[a]

Period/Cycle/Location	Bromobenzene	1-Chloro-2-Bromoethane	1,2-Dibromo-ethane	Dibromochloro-propanes	Bromoform	1-Chloro-3-Bromopropene	Bromodichloro-methane	Allyl bromide	Bromopropanes	Dibromopropanes	Chlorodibromo-methane	Dibromomethane
P1/C1/L1	5.3	ND	1.7	ND	ND	ND	T	ND	ND	N	N	ND
P2/C1/L1	ND	ND	95	ND	T	ND	T	ND	T	ND	ND	ND
L2	470	73	271,283	1.4	25	ND	T	ND	T	ND	ND	ND
L3	3,842	70	2,408	1.4	20	T	ND	T	ND	T	ND	ND
L4	188	34	20	ND	ND	ND	ND	ND	T	ND	ND	ND
L5	1,131	2.8	T	T	22	ND	ND	ND	ND	ND	ND	ND
P3/C1/L1	ND	ND	2.8	T	T	T	T	T	T	ND	ND	ND
L2	29	T	8,092	T	T	ND	T	ND	ND	ND	ND	ND
L3	4,276	ND	39,060	T	T	ND	ND	ND	ND	ND	ND	ND
L4	20	ND	3,352	T	T	ND	ND	ND	T	ND	ND	ND
L5	51	ND	32,872	2.8	98	ND	T	ND	ND	ND	ND	ND
P4/C1/L1	ND	T	ND	T	ND	ND	ND	ND	ND	ND	ND	ND
L2	280	ND	118	ND	T	T	T	ND	ND	T	ND	ND
L3	1,041	T	896	ND	104	ND	T	T	ND	T	ND	ND
L4	22	ND	190	ND	ND	ND	ND	T	ND	ND	ND	ND
L5	980	22	35,056	5.6	37	ND	T	ND	ND	T	ND	ND

(continued)

Table 6.6 (cont'd)

Period/Cycle/Location	Bromobenzene	1-Chloro-2-Bromoethane	1,2-Dibromoethane	Dibromochloropropanes	Bromoform	1-Chloro-3-Bromopropene	Bromodichloromethane	Allyl bromide	Bromopropanes	Dibromopropanes	Chlorodibromomethane	Dibromomethane
P5/C1/L1	4.5	ND	T	T	ND	ND	ND	T	T	T	ND	ND
L2	428	T	1,056	ND	T	T	T	ND	ND	ND	ND	ND
L3	95	ND	526	ND	22	T	ND	T	T	ND	ND	ND
L4	4.8	ND	T	ND	T	ND	ND	ND	ND	T	ND	ND
L5	4.8	T	270	T	T	T	ND	ND	T	T	T	ND

[a] Values are in ng/m^3.

Bromobenzene, 1-chloro-2-bromoethane, dibromochloropropanes and bromoform were also measured. Trace levels of several other brominated organics were detected. However, in contrast to the survey sampling phase, chlorodibromomethane and dibromomethane were not detected.

Tables 6.7 and 6.8 present the concentration of ethylene in ambient air surrounding the Great Lakes Chemical Corp. plants in El Dorado and Marysville. The background levels of ethylene were approximately 1 ppm and, in some cases, reached 6-7 ppm at locations 3 and 4 at the El Dorado plant site. Elevated concentrations of ethylene were not detected at the Marysville plant.

Analysis of the particulate material collected on Hi-Vol glass fiber filters revealed the presence of traces of tetrabromobisphenol A (Table 6.9). The highest level was observed during the fourth sampling period when it reached 1.8 $\mu g/m^3$. Also at this time Decabrom was detected at a level of 25 $\mu g/m^3$. This sampling period generally favored a downwind position from the Tetrabrom facility.

Sediment.--Samples of sediment which were selected for analysis did not contain detectable levels of pentabromophenol. However, relatively large quantities of Tetrabrom and Decabrom were found (Table 6.10). In fact, these samples represented the most contaminated of those examined. A level of 1 g/kg of Decabrom was found in sediment taken from near an "outfall pipe" which presumably came from Great Lakes Chemical Corp.

Soil.--Pentabromophenol was quantified in a soil sample taken ~1 mile off property of Great Lakes Chem. Significant quantities of Tetrabrom and Decabrom were found in other soil samples, one of which (L4) contained 150 mg/kg and 25 mg/kg of these chemicals, respectively (Table 6.11).

6.2.2 Michigan Chemical Corporation (Velsicol) and Vicinity

6.2.2.1 Sampling

The ambient air sampling protocol for Velsicol Chemical Corporation in El Dorado, AK is given in Table 6.12. A schematic map of Velsicol showing the air sampling locations is given in Figure 6.6. Table 6.13 presents the sampling protocols for water and sediment surrounding and on Velsicol, Inc. Figures 6.7 and 6.8 present the water and sediment sampling locations. Table 6.14 presents the soil sampling protocol and Figures 6.9 and 6.10, the

Table 6.7. CONCENTRATIONS OF ETHYLENE IN AMBIENT AIR SURROUNDING GREAT LAKES CHEMICAL CORP.

Period/Cycle/Location	ppm Ethylene
P4/C1/L1	4.4
P4/C1/L2	1.0
P4/C1/L3	7.2
P4/C1/L4	6.3
P4/C1/L5	4.8
P4/C1/L9	2.6
Lab-1[a]	0.1
Lab-2[a]	2.2
Field-1[b]	0.3
Field-2[b]	0.9
Field-3[b]	0.4
Lab-1[a,c]	3.8
Lab-2[a,d]	10.1
Field-1[b,c]	1.7
Field-2[b,c]	4.9
Field-3[b,d]	6.5
Field-4[b,d]	10.0

[a] Stored @ 4°C in the lab.

[b] Transported to the sampling area and returned to the lab.

[c] Spiked with 0.9 ppm ethylene.

[d] Spiked with 9.7 ppm ethylene.

Table 6.8. CONCENTRATIONS OF ETHYLENE IN AMBIENT AIR SURROUNDING GREAT LAKES CHEMICAL, INC. - MARYSVILLE PLANT

Period/Cycle/Location	ppm Ethylene
P1/C1/L2	1.4
P1/C1/L3	1.1
P1/C1/L4	2.1
P1/C1/L5	1.7
Lab-1[a]	0.1
Lab-2[a]	2.2
Field-1[b]	0.3
Field-2[b]	0.9
Field-3[b]	0.4
Lab-1[a,c]	3.8
Lab-2[a,d]	10.1
Field-1[b,c]	1.7
Field-2[b,c]	4.9
Field-3[b,d]	6.5
Field-4[b,d]	10.0

[a] Stored at 4°C in the lab.

[b] Transported to the sampling area and returned to the lab.

[c] Spiked with 0.9 ppm ethylene.

[d] Spiked with 9.7 ppm ethylene.

Table 6.9. RESULTS OF THE ANALYSIS OF HI-VOL FILTERS FOR SEMI-VOLATILE BROMINATED ORGANICS - GREAT LAKES CHEMICAL CORPORATION, EL DORADO, ARKANSAS

Period/Cycle/Location[a]	Tetrabromobisphenol A[b] (μg/m^3)	Decabromobiphenyl ether (μg/m^3)
P2/C1/L5	0.08[c]	8.0[c]
P3/C1/L5	1.2[c]	1.0[c]
P4/C1/L5	1.8[c,d]	25[c,e]
P5/C1/L5	ND[c]	2.0[c]

[a] See Table 6.2 and Figure 6.2 for locations of samples.

[b] 2,2'-Bis(dibromo-4-hydroxyphenyl)propane.

[c] Quantitation by gas chromatography-mass spectrometry with multiple ion detection.

[d] Confirmed by ion intensity ratio of 1.7 for the sample vs. 1.5 for the standard for 529/531.

[e] Confirmed by ion intensity ratio for the sample of 2.8 compared to 2.7 for the sample for ion pair 800/804.

Table 6.10. RESULTS OF ANALYSIS OF SEDIMENT SAMPLES FOR SEMI-VOLATILE BROMINATED ORGANICS GREAT LAKES CHEMICAL CORPORATION, EL DORADO, ARKANSAS

Period/Cycle/Location[a]	Pentabromophenol (μg/Kg)	Tetrabromobisphenol A[b] (μg/Kg)	Decabromobiphenyl ether (μg/Kg)
P4/C1/L5	ND[c,d]	630[d]	ND[c,d]
P4/C1/L8	ND[d]	24,000[d]	14,000[d]
P5/C1/L10	-	-	1,000,000[e]
P5/C1/L13	ND[d]	330,000[d]	6,300[d]
P6/C1/L14	ND[d]	300[d]	ND[d]

[a] See Table 6.4 and Figure 6.4 for locations of samples.

[b] 2,2'-Bis(dibromo-4-hydroxyphenyl)propane.

[c] Not detected - approximately 100 μg/Kg is required to detect these compounds.

[d] Quantitation by gas chromatography - mass spectrometry using multiple ion detection.

[e] Quantitation by thin layer chromatography.

Table 6.11. RESULTS OF ANALYSIS OF SOIL SAMPLES FOR SEMI-VOLATILE BROMINATED ORGANICS GREAT LAKES CORPORATION, EL DORADO, ARKANSAS

Period/Cycle/Location	Pentabromophenol (μg/Kg)	Tetrabromobisphenol A[b] (μg/Kg)	Decabromobiphenyl ether (μg/Kg)
P1/C1/L1	ND[c]	ND[c]	ND[c]
P4/C1/L4	ND	150,000[e]	25,000[d]
P4/C1/L7	ND	8,000	1,400
P8/C1/L18	200	2,000	120
P8/C1/L20	ND	ND	ND

[a] See Table 6.3 and Figure 6.1 for location of samples.

[b] 2,2'-Bis(dibromo-4-hydroxyphenyl)propane.

[c] Not detected - approximately 50 μg/kg is required for detection of these compounds.

[d] Quantitation by gas chromatography/mass spectrometry using multiple ion detection.

[e] Identity confirmed by full scan gc/ms analysis.

Table 6.12. AMBIENT AIR SAMPLING PROTOCOL SURROUNDING VELSICOL CHEMICAL CORP., EL DORADO, AK

Period	Cycle	Location	Sampling Time	Sampling Volume (ℓ)	Type of Sample	Meteorological Conditions T(°C)	 %RH	 Wind Direction Speed (kmph)	 Other
P1 7/22/77	C1	L1	1130-0925 (9/23/77)	179	HHC^{ab}				
		L2	1140-0945 (9/23/77)	<162	HHC^{ab}	18-38			
		L3	1205-1000 (9/23/77)	191	HHC^{ab}		52-88	NW-5-8 (4 hrs.)	Pump stopped
		L4	1105-1015 (9/23/77)	81	HHC^{ab}			S/0-3 (18 hrs.)	
		L5	1220-1040 (9/23/77)	116	HHC^{ab}				
		L1	1010-1455	205	CBD,CBN^{c}				
		L2	1016-1500	216	CBD,CBN^{c}				
		L3	1025-1504	249	CBD,CBN^{c}			Variable	Bromine upset ~1045
		L4	1031-1507	221	CBD,CBN^{c}			SE,W,NW,/7	
		L1	1547	0.5	VAC				
		L2	1550	0.5	VAC				
		L6	1540	0.5	VAC				
		L7	1554	0.5	VAC				
		L8	1600	0.5	VAC				
		L4	1115-1025 (9/23/77)	1,573,000	Hi-Vol				
P2 7/23/77	C1	L1	0935-0925 (9/24/77)	138	HHC^{ab}				
		L2	1400-0945 (9/24/77)	150	HHC^{ab}	21-40	50-92	N,NW,variable/0-8 (13 hrs.)	
		L3	1010-1000 (9/24/77)	150	HHC^{ab}			S/2-8 (12 hrs.)	
		L4	1020-1010 (9/24/77)	26	HHC^{ab}				
		L5	1040-1025 (9/24/77)	114	HHC^{ab}				
		L1	0930-1350	214	CBD,CBN^{c}				
		L2	0945-1355	187	CBD,CBN^{c}			Variable/3-5	
		L3	1000-1405	247	CBD,CBN^{c}				
		L4	1015-1405	197	CBD,CBN^{c}				
		L1	0930	0.5	VAC				
		L2	0950	0.5	VAC				
		L3	1005	0.5	VAC				
		L4	1018	0.5	VAC				
		L5	1040	0.5	VAC				
		L4	1030-1010 (9/24/77)	1,587,000	Hi-Vol				

(continued)

Table 6.12 (cont'd)

						Meteorological Conditions			
Period	Cycle	Location	Sampling Time	Sampling Volume (ℓ)	Type of Sample	T(°C)	%RH	Wind Direction Speed (kmph)	Other
P3 7/24/77	C1	L1	0940-1002 (9/25/77)	121	HHC[ab]				
		L2	0950-1017 (9/25/77)	176	HHC[ab]	21-38	45-92	S/3-11 (15 hrs.)	
		L3	1005-1033 (9/25/77)	149	HHC[ab]			NE,N/4-5 (5 hrs.)	
		L4	1055-1045 (9/25/77)	97	HHC[ab]			Variable/5 (5 hrs.)	
		L5	1055-1040 (9/25/77)	26	HHC[ab]				
		L1	0925-1400	224	CBD,CBN[c]			S, variable/4-7	
		L2	0945-1402	189	CBD,CBN[c]				
		L3	1005-1405	208	CBD,CBN[c]				
		L4	1018-1410	199	CBD,CBN[c]				
		L4	1015-1040	1,617,000	Hi-Vol				
P4 7/25/77	C1	L1	1010-1019 (7/26/77)	218	HHC[ab]	20-37	56-90	S,SE/2-12 (~16 hrs.)	
		L2	1026-0830 (7/26/77)	<200	HHC[ab]			NE/4-10 (~5 hrs.)	Pump stopped
		L3	1040-0840 (7/26/77)	170	HHC[ab]				
		L4	1055-0850 (7/26/77)	119	HHC[ab]				
		L1	1005-1432	218	CBD,CBN[c]			S,SE/10-12	
		L2	1025-1436	181	CBD,CBN[c]				
		L3	1045-1440	206	CBD,CBN[c]				
		L4	1052-1445	188	CBD,CBN[c]				
		L1	1005	0.5	VAC				
		L2	1023	0.5	VAC				
		L3	1035	0.5	VAC				
		L4	1055	0.5	VAC				
		L5	1100	0.5	VAC				
		L4	1050-0850 (7/26/77)	1,438,000	Hi-Vol				

[a] DuPont sampler 3-6 ft elevation.

[b] Overnight sampling.

[c] Nutech Model 220 sampler 3-6 ft elevation.

Locations shown in Figure 6.6.

Key to Sample Type:

HHC - Halogenated Hydrocarbon
CBN - Bromine and Chlorine
CBD - Bromide and Chloride
VAC - Aluminum Vacuum Can

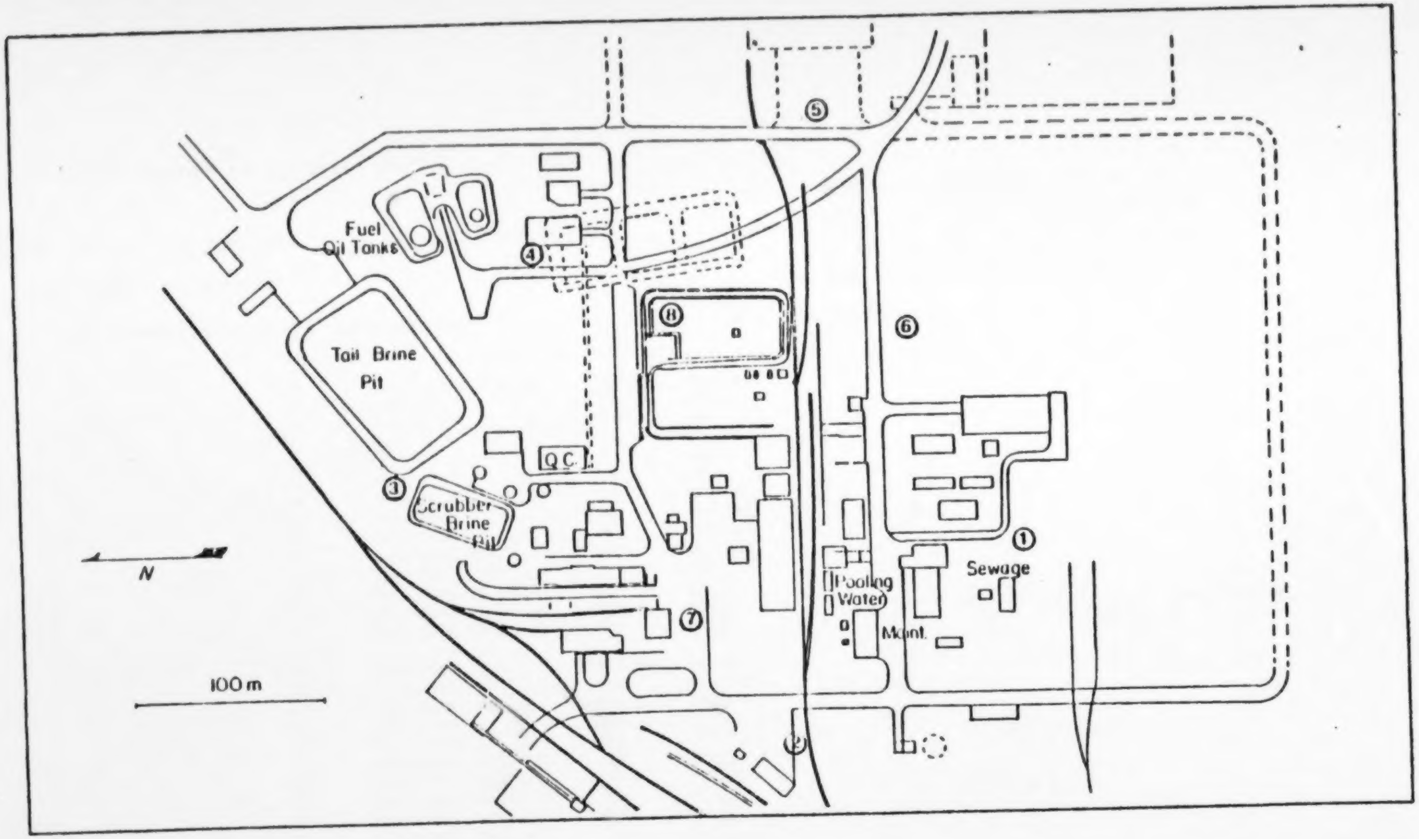

Fuel
Oil Tanks
Tail Brine
Pit
Scrubber
Brine
Pit
Q.C.
Cooling
Water
Maint.
Sewage
①
②
③
④
⑤
⑥
⑦
⑧
N
100m

Figure 6.6. Schematic map of Velsicol, Inc., El Dorado, AK. Air sampling locations P1 (7/22/77) through P4 (7/25/77).

Table 6.13. WATER AND SEDIMENT SAMPLING PROTOCOL SURROUNDING AND ON VELSICOL, INCORPORATED, EL DORADO, ARKANSAS

Period	Cycle	Location	Sample Type	Sample Size (ℓ)	Comments
P1 7/22/77	C1	L1	W/HHC^a SD/HHC^a	2 2	∿1/2 km north of plant in power line corridor
		L2	W/HHC^a	2	Sessile water
		L3	W/HHC^a	2	Walker Creek
P2 7/23/77	C1	L4	W/HHC^b SD/HHC^b	2 2	∿400 m west of Firemaster 680 facility
P4 7/25/77	C1	L5	W/HHC^a SD/HHC^a	2 2	Creek dried up except for a puddle

[a] See Figure 6.7 for map of sample locations.

[b] See Figure 6.8 for map of sample locations.

W = water
SD = sediment
HHC = for halogenated hydrocarbon analysis

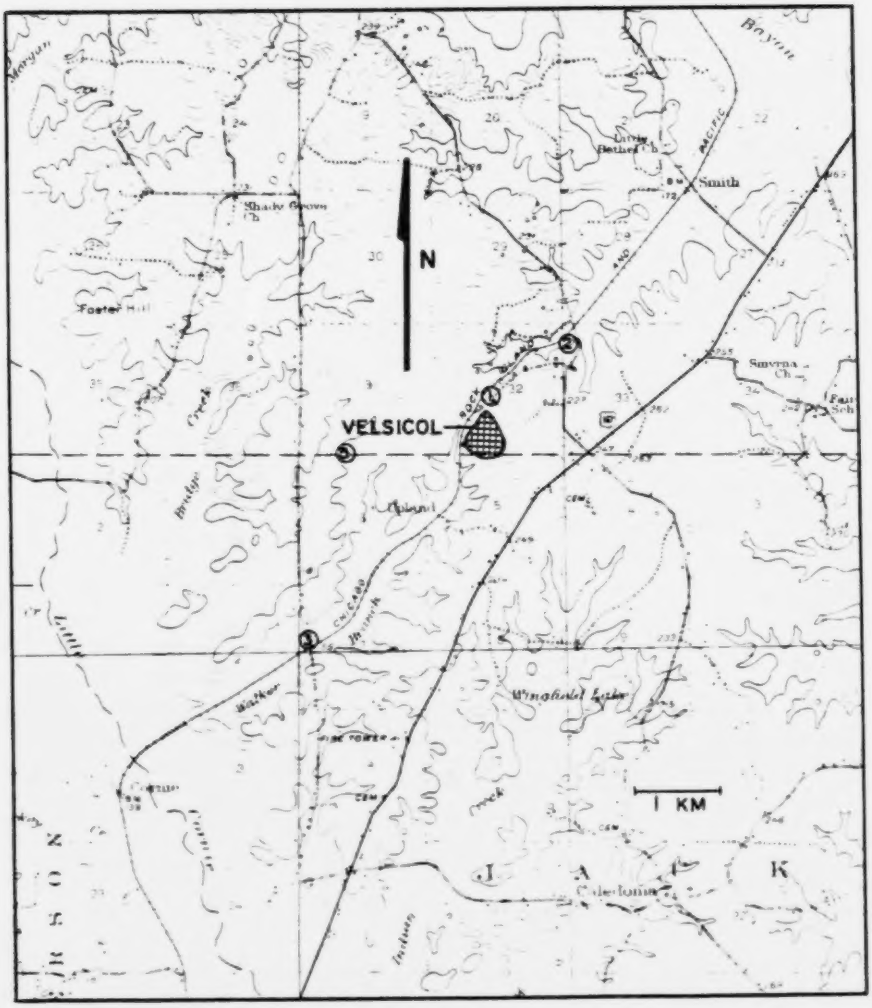

N
VELSICOL
①
②
③
⑤
1 KM
Bayou
Smith
Little Bethel Ch
Shady Grove Ch
Foster Hill
Smyrna Ch
Bridge Creek
Upland
Chicago Rock
Walker
Wingfield Lake
Fire Tower
Caledonia
Indian
Creek
L A K

Figure 6.7. Vicinity map of Velsicol, Inc., El Dorado, Arkansas - Water and sediment sample locations (7/22/77 - 7/25/77).

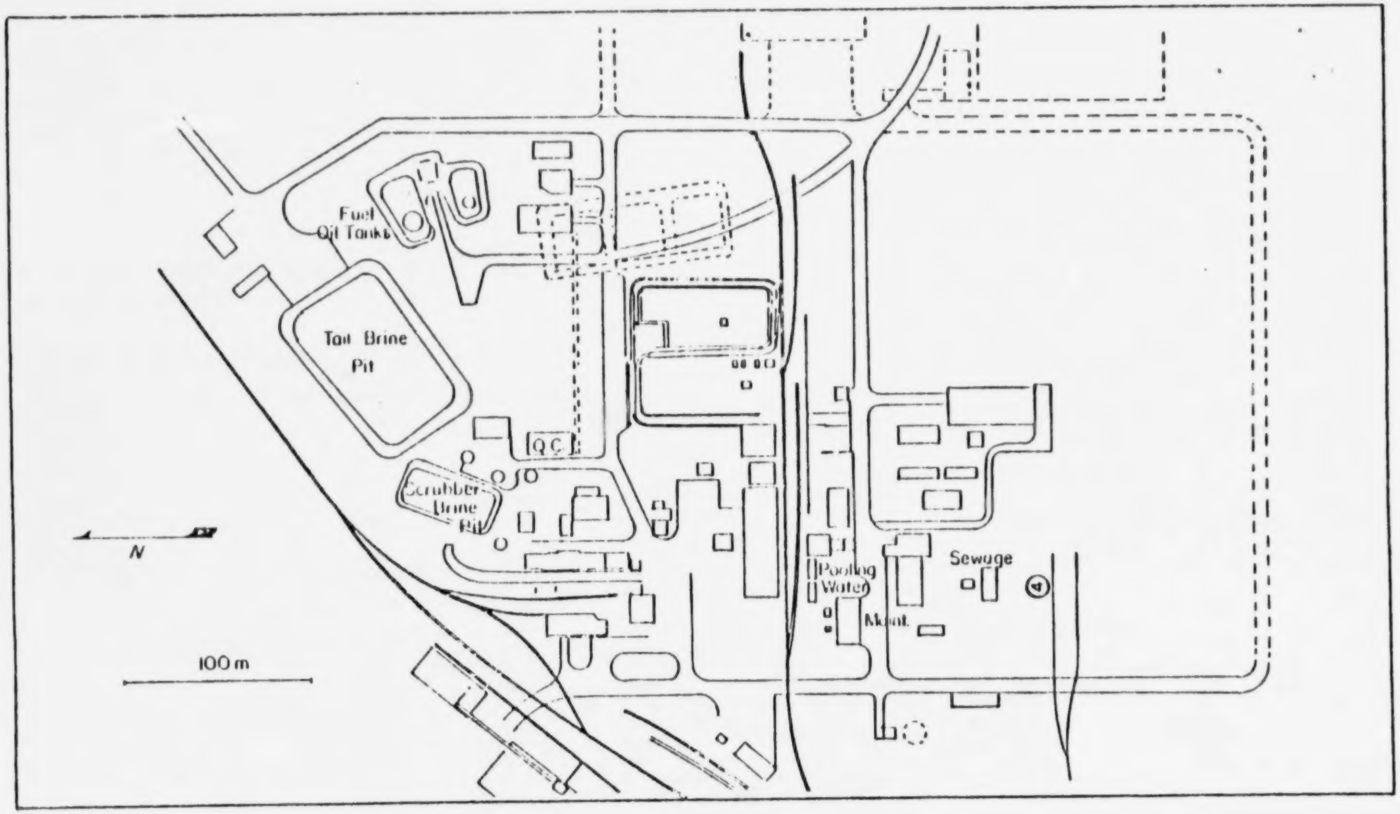

Fuel
Oil Tanks
Tail Brine
Pit
QC
Scrubber
Brine
Pit
Pooling
Water
Maint.
Sewage
4
N
100 m

Figure 6.8. Schematic map of Velsicol, Inc., El Dorado, Arkansas - Water and sediment sampling location (7/23/77).

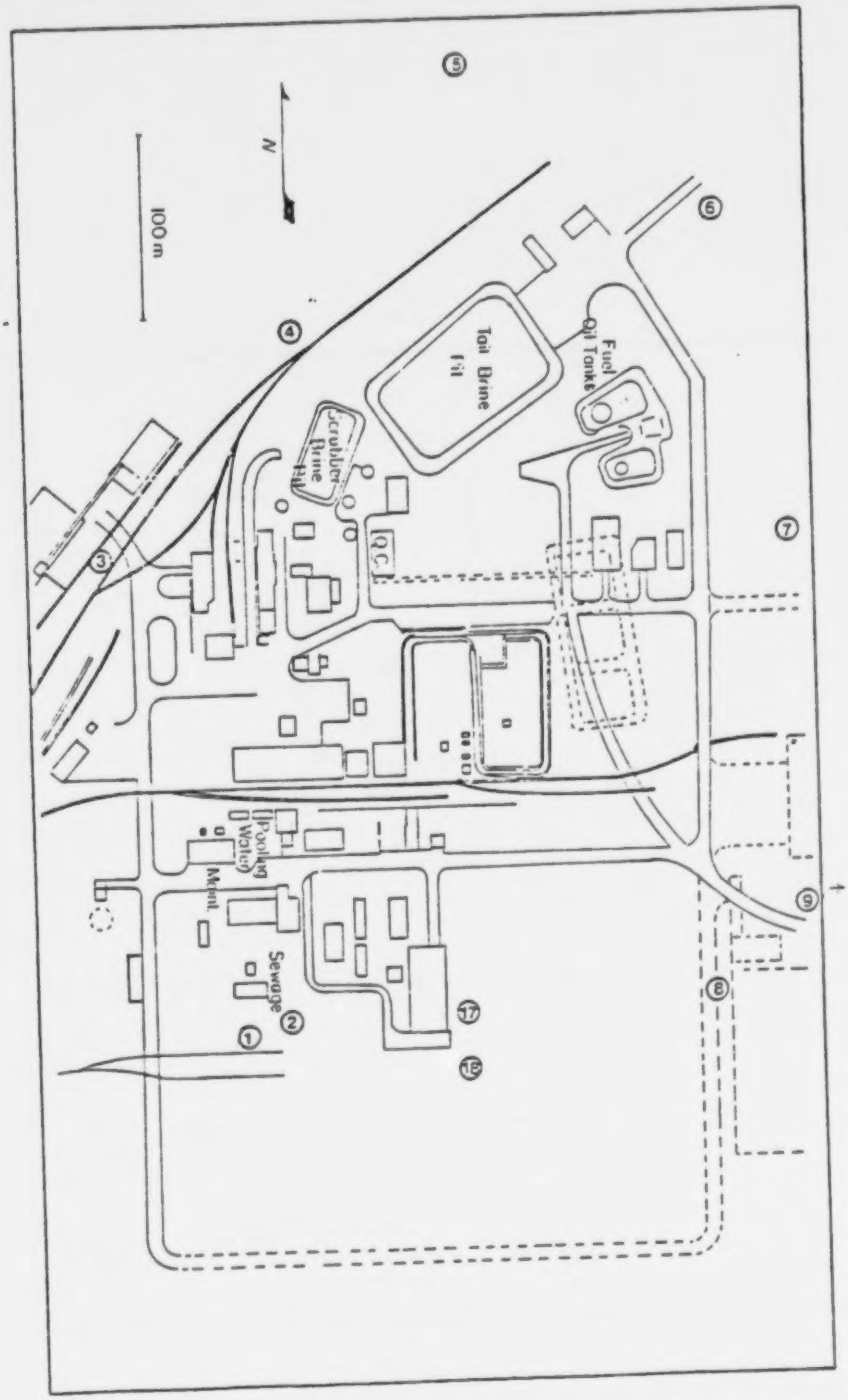
Table 6.14. SOIL SAMPLING PROTOCOLS SURROUNDING AND ON VELSICOL, INC., EL DORADO, ARKANSAS

Period	Cycle	Location	Sample Type	Sample Size	Comments
P1 7/22/77	C1	L1	S/HHC[a]	2 cores	Near r.r. tracks (fill dirt).
		L2	S/HHC[a]	2 cores	Between r.r. tracks and sewage treatment facility in a dry stream bed.
		L3	S/HHC[a]	2 cores	Near r.r. tracks.
		L4	S/HHC[a]	2 cores	Near r.r. tracks.
		L5	S/HHC[a]	2 cores	In power line right of way - woods on either side.
		L6	S/HHC[a]	2 cores	Near a service road.
		L7	S/HHC[a]	2 cores	West of plant beyond a fill area - woods on west side of location.
		L8	S/HHC[a]	2 cores	Near service road.
		L9	S/HHC[a]	2 cores	From clearing next to car wash at entrance.
		L10	S/HHC[b]	2 cores	~500 M from bromine extraction in power line corridor.
		L11	S/HHC[b]	2 cores	~20 M north of road in a grassy area.
		L12	S/HHC[b]	2 cores	~2 KM WSW of Velsicol on trail through woods.
		L13	S/HHC[b]	2 cores	Between dirt road and r.r. tracks near power substation.
P2 7/23/77	C1	L14	S/HHC[b]	2 cores	~1/2 KM east of plant at a power substation.
		L15	S/HHC[b]	2 cores	~1/2 KM north of plant.
		L16	S/HHC[b]	2 cores	~2 KM due south of plant.
P4 7/25/77	C1	L17	S/HHC[a]	2 cores	From ditch with water probably run off next to Firemaster 680 warehouse.
		L18	S/HHC[a]	2 cores	From the hill above the ditch (L17).
		L19	S/HHC[b]	2 cores	~1 KM due east of plant on power line right of way.

[a] See Figure 6.9 for map of sample locations.

[b] See Figure 6.10 for map of sample locations.

S = soil sample
HHC = for halogenated hydrocarbon analysis



⑤
N
100m
⑥
④
Fuel Oil Tanks
Tail Brine Pit
Scrubber Brine Pit
Q.C.
⑦
③
Pooling Water
Maint.
Sewage
⑨
⑧
⑰
②
①
⑱

Figure 6.9. Schematic map of Velsicol, Inc., El Dorado, Arkansas - Soil sampling locations (7/22/77 to 7/25/77).

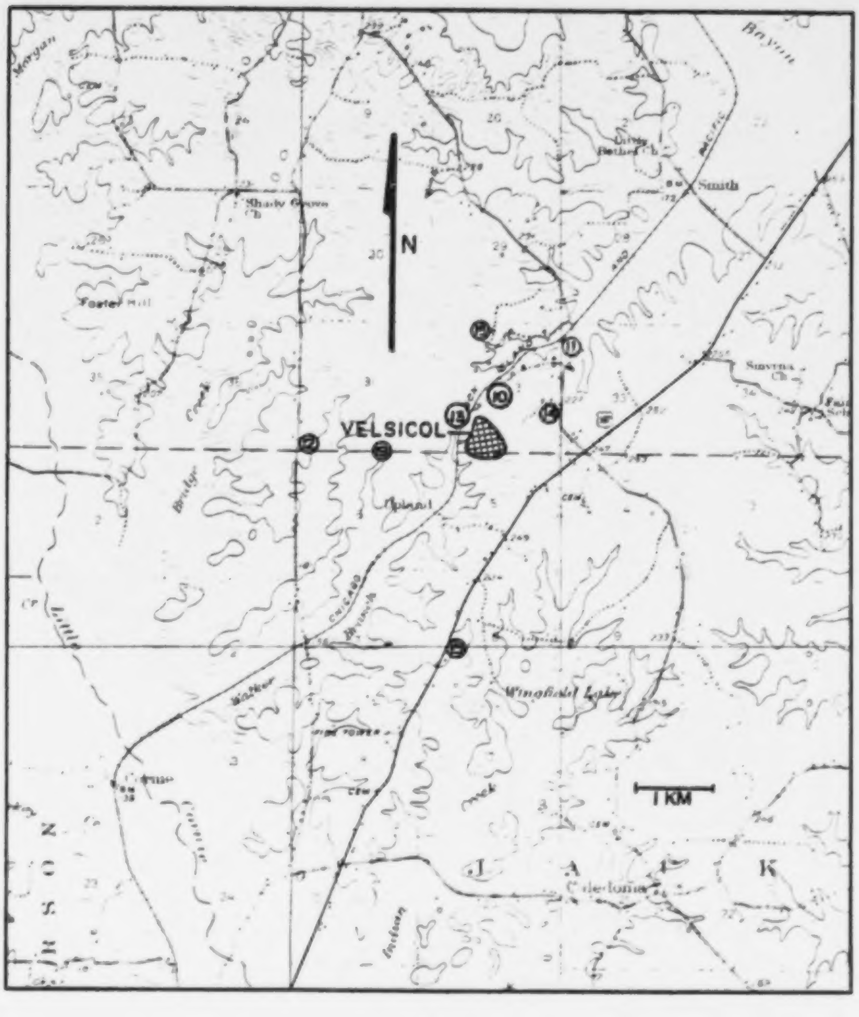

N
VELSICOL
10
11
1 KM
Bayou
Smith
Foster Hill
Shady Grove
Smyrna
CHICAGO
Wingfield Lake
Caledonia

Figure 6.10. Vicinity map of Velsicol, Inc., El Dorado, Arkansas - Soil sampling locations (7/22/77 to 7/25/77).

corresponding sampling locations. Table 6.15 gives the sampling protocols for the biota which were taken surrounding and on Velsicol, Inc. while Figures 6.11 and 6.12 depict the locations of sampling.

6.2.2.2 Inorganics in Ambient Air

Table 6.16 gives the concentrations of halides and halogens in ambient air surrounding Velsicol. The samples were selected for analysis on the basis of meteorological conditions. The detection limit for halide was approximately <10 $\mu g/m^3$. The highest halide level detected occurred during the fourth sampling period at L3 when a level of 91 $\mu g/m^3$ was reached. The concentration of halogen, on the other hand, was observed to be 219 $\mu g/m^3$ at the third location during the third sampling period. Inspection of these data indicate a concomitant increase and decrease in the levels of halides and halogen during the various sampling periods.

6.2.2.3 Brominated and Other Organics

Air.--The ambient air levels of volatile brominated organics surrounding Velsicol, Inc. are given in Table 6.17. Many brominated organics which were detected during the Survey Phase (see Section 4.2.3.5) were not detected during this phase. Ethylene dibromide, dibromochloropropane (DBCP) and chlorodibromomethane were detected at relatively low concentrations throughout each of the four sampling periods.

Table 6.18 gives the concentrations of ethylene in ambient air. Recalling that the background concentration is ~0.6 - 1.0 ppm, the highest level of ethylene was found at L7 at which time it reached 6.8 ppm.

The glass fiber filters were analyzed according to the procedures in Appendix A for semi-volatile brominated organics. The results are presented in Table 6.19. With the particulate samples collected by Hi-Vol samplers the interpretation of a positive finding is complicated by the possibility that the compounds found may not be current emissions. They may be adsorbed onto soil particles which continue to be resuspended in the air. The primary counterindication of the above is the presence of varying combinations of material from day to day especially TRIS and Firemaster 680 with very similar meteorology.

A control filter was spiked with TRIS, Tetrabrom and Decabrom using a matrix of 10 cm^2 (2 cm x 5 cm) alternating spiked areas with blank areas. A

Table 6.15. VEGETATION AND MISCELLANEOUS SAMPLING PROTOCOLS SURROUNDING AND ON VELSICOL, INC., EL DORADO, ARKANSAS

Period	Cycle	Location	Sample Type	Sample Size (ℓ)	Comments
P1 7/22/77	C1	L1	V/HHC[a]		Fern type leaves
		L2	V/HHC[a]		
		L3	V/HHC[b]		Corn
		L4A	V/HHC[b]		Tomato
		L4B	V/HHC[b]		Cabbage
P2 7/23/77	C1	L5	M/HHC[b]	0.5	Cow's milk

[a] See Figure 6.11 for map of sample locations.

[b] See Figure 6.12 for map of sample locations.

V = vegetation
M = miscellaneous samples
HHC = for halogenated hydrocarbon analysis

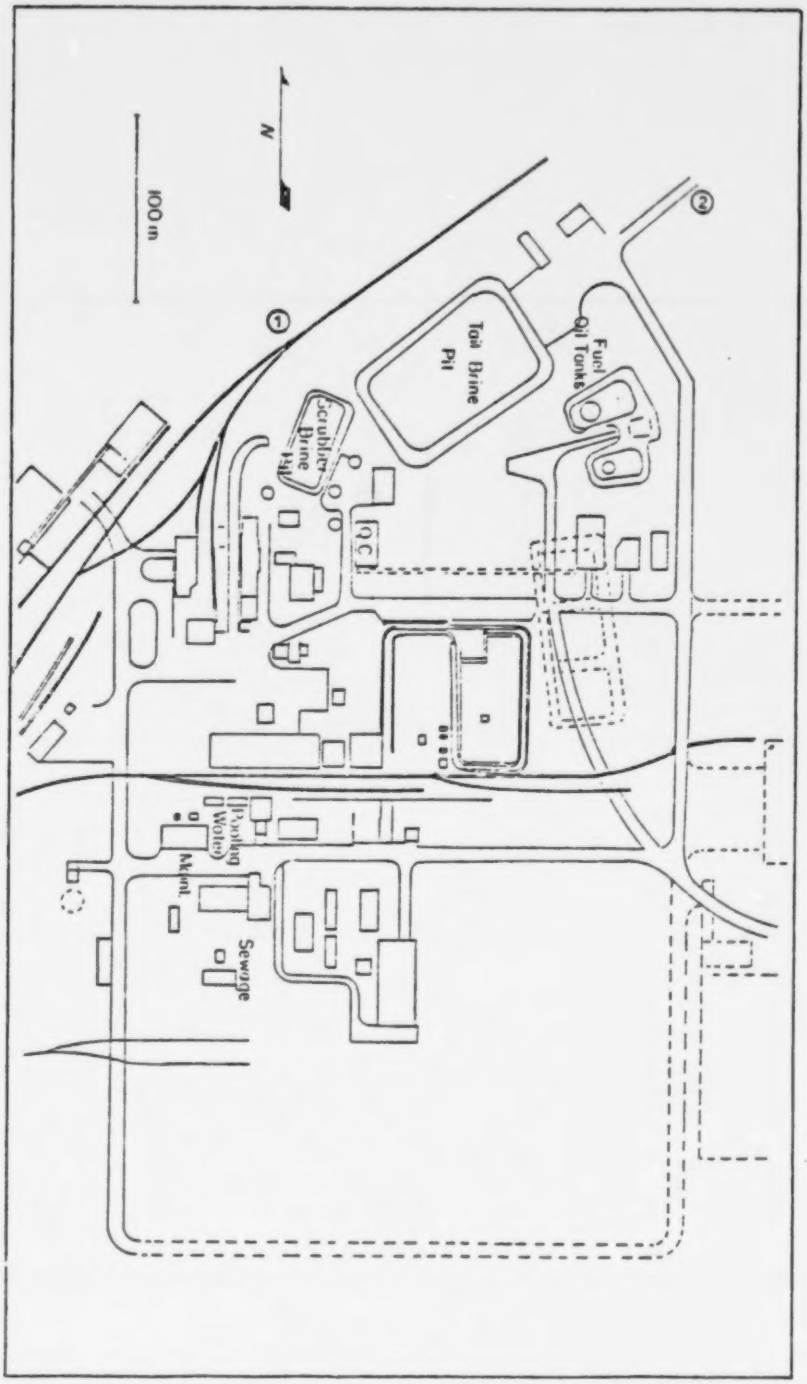

100 m
N
①
②
Fuel Oil Tanks
Tail Brine Pit
Scrubber Brine Pit
Cooling Water
Maint.
Sewage

Figure 6.11. Schematic map of Velsicol, Inc., El Dorado, Arkansas - Vegetation and miscellaneous sampling locations (7/22/77 - 7/23/77).

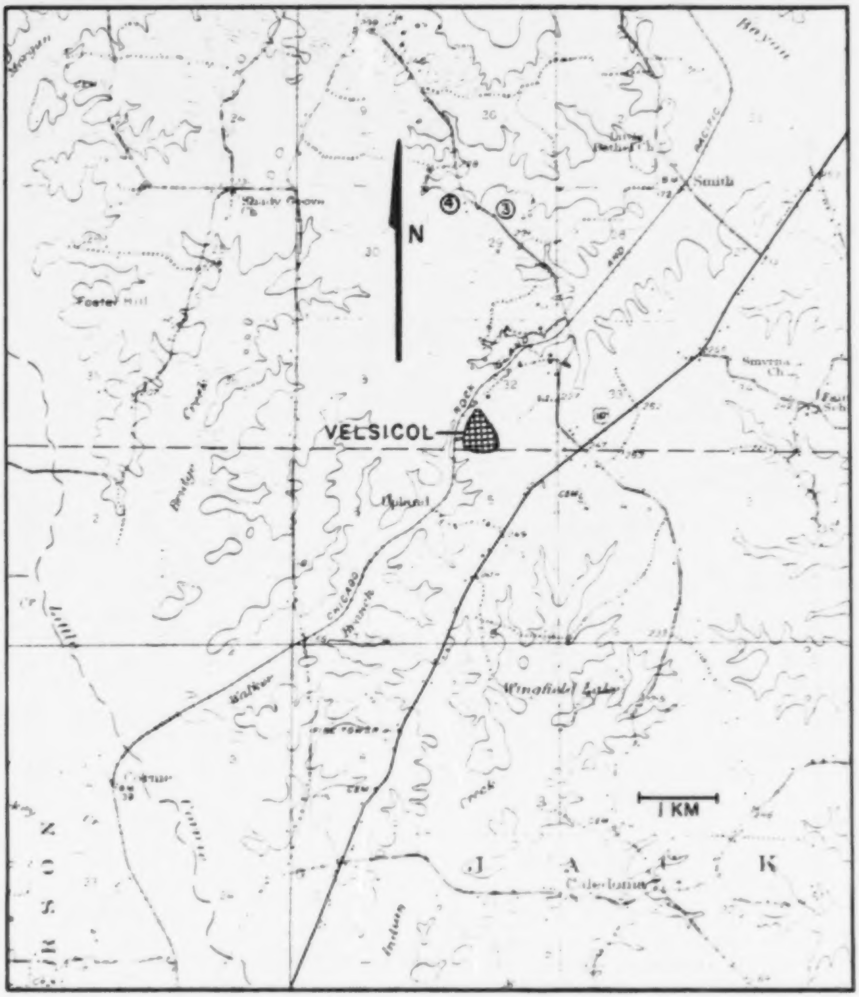

N
④
③
VELSICOL
1 KM
Smith
Bayou
Foster Hill
Upland
Wingfield Lake
Caledonia
Smyrna Ch.
Creek
Walker
J A K

Figure 6.12. Map of the vicinity of Velsicol, Inc., El Dorado, Arkansas - Vegetation and miscellaneous sample locations (7/22/77 - 7/23/77).

Table 6.16. HALIDES AND HALOGENS QUANTITATED IN AMBIENT AIR SURROUNDING VELSICOL, INC., EL DORADO, AK

Period/Cycle/Location[a]	Halide as Cl^{-b} μg/m^3	Halogen as Cl_2[b] μg/m^3
P1/C1/L1	83 ± 18	41 ± 10
L3	27 ± 6	75 ± 45[c]
L4	51 ± 7	75 ± 30
P2/C1/L1	<21	< 8
L3	35 ± 7	81 ± 38[c]
L4	<18	<20
P3/C1/L1	<15	<17
L3	63 ± 8	219 ± 9
L4	<10	<20
P4/C1/L1	< 8	41 ± 16
L3	91 ± 8	158 ± 44[c]
L4	<18	74 ± 21

---

[a] Refer to Table 6.12 for sampling protocol.

[b] Values are expressed as Cl^- or Cl_2. However, if Br^- or Br_2 is the predominant species, the values should be multiplied by 1.5.

[c] An amber color developed when $AgNO_3$ was added in the procedure.

Table 6.17. AMBIENT AIR LEVELS OF VOLATILE BROMINATED ORGANICS SURROUNDING VELSICOL CHEMICAL CORP., EL DORADO, AK[a]

Period/Cycle/Location	1,2-Dibromoethane	Dibromochloro-propane	Bromoform	1-Chloro-3-bromo-propane	Bromodichloro-methane	Allyl bromide	Bromopropanes	Dibromopropanes	Chlorodibromo-methane	Dibromomethane
P1/C1/L1	493	93	ND	ND	ND	ND	ND	ND	ND	ND
L2	227 ± 45	174	T	ND	ND	ND	ND	ND	8.4 ± 2.8	ND
L3	501	7.8	T	ND	ND	ND	ND	ND	ND	ND
L4	45	34	ND	ND	ND	ND	ND	ND	T	ND
L5	448	14	ND	ND	ND	ND	ND	ND	31	ND
P2/C1/L1	T	12	ND	ND	ND	ND	ND	ND	ND	ND
L2	868	187	T	ND	ND	ND	ND	ND	T	ND
L3	T	37	ND	ND	ND	ND	ND	ND	ND	ND
L4	280	32	T	ND	ND	ND	ND	ND	T	ND
L5	120	T	ND	ND	ND	ND	ND	ND	22	ND
P3/C1/L1	T	ND	T	ND	ND	ND	ND	ND	T	ND
L2	T	T	ND	ND	ND	ND	ND	ND	23	ND
L3	2,425	T	T	ND	ND	ND	ND	ND	ND	ND
L4	ND	T	ND	ND	ND	ND	ND	ND	81	ND
L5	342	T	ND	ND	ND	ND	ND	ND	ND	ND
P4/C1/L1	67	ND	ND	ND	ND	ND	ND	ND	ND	ND
L2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
L3	193	T	ND	ND	ND	ND	ND	ND	ND	ND
L4	171	T	ND	ND	ND	ND	ND	ND	ND	ND

[a] Values are in ng/m^3

Table 6.18. CONCENTRATIONS OF ETHYLENE IN AMBIENT AIR SURROUNDING VELSICOL CHEMICAL INC.

Period/Cycle/Location	ppm Ethylene
P1/C1/L1	0.6
P1/C1/L2	3.8
P1/C1/L6	2.3
P1/C1/L7	6.8
P1/C1/L8	5.3
Lab-1[a]	0.1
Lab-2[a]	2.2
Field-1[b]	0.3
Field-2[b]	0.9
Field-3[b]	0.4
Lab-1[a,c]	3.8
Lab-2[a,d]	10.1
Field-1[b,c]	1.7
Field-2[b,c]	4.9
Field-3[b,d]	6.5
Field-4[b,d]	10.0

[a] Stored at 4°C in the laboratory.

[b] Transported to the sampling area and returned to the lab.

[c] Spiked with 0.9 ppm ethylene.

[d] Spiked with 9.7 ppm ethylene.

Table 6.19. BROMINATED ORGANICS FOUND ON GLASS FIBER FILTERS FROM HI-VOL SAMPLERS

Period/Cycle/Location	Tetrabromobis-phenol A ng/m^3	Firemaster 680 ng/m^3	Tris(2,3-dibromo-propyl)phosphate ng/m^3	Decabromobiphenyl ether ng/m^3
P1/C1/L4	28[a,b]	39[a,c]	60[d]	ND
P2/C1/L4	ND[a]	ND[a]	44[d]	ND[a]
P3/C1/L4	ND[a]	172[a,c]	51[d]	ND[a]
P4/C1/L4	ND[a]	183[a,c]	ND[d]	72[a,c]

[a] GLC/MS/COMP analysis in the multiple ion detection mode.

[b] Ion intensity ratio of m/e 529/531 was 1.42 *vs*. 1.48 for standard tetrabromobisphenol A.

[c] One ion monitored, no confirmation.

[d] Analysis by GLC/ECD. Results are uncorrected for recovery which was 87% at an equivalent to 27 ng/m^3 and 91% at an equivalent to 287 ng/m^3 of TRIS.

24 hr Hi-Vol air sample of 2000 m^3 was collected at RTI, RTP. Recoveries of 2 areas analyzed for TRIS are given in Table 6.20.

Table 6.20. TRIS RECOVERY STUDY

Amount of TRIS added (μg)	Amount of TRIS found[a] (μg)	% Recovered
11.1	10.2	91
1.04	0.90	87

[a] Analysis by GLC/ECD.

This filter was transported to the field and returned before analysis.

Water and Sediment.--Water samples P1/C1/L1 and P4/C1/L5 (see Table 6.13 and Figures 6.6 and 6.8) were analyzed by the VOA method for qualitative information. No brominated compounds were identified by this method.

Water and sediment samples from Velsicol were analyzed for semi-volatile brominated organics according to the protocol in Appendix A. The results are shown in Table 6.21. The TRIS found in the water sample P1/C1/L3 is indicative of water transport since the creek sampled is part of the Velsicol watershed. The origin of Firemaster 680 and TRIS at P4/C1/L5 is less obvious. This location is 1.5 km from the facility and airborne contamination may contribute. The watershed for this stream extends to within 0.6 km of the facility. At the time the sample was collected drought had reduced the stream to a pool approximately 2 x 5 m. The combination of airborne dispersion and collection and dispersion of runoff water may have resulted in the TRIS and Firemaster 680 levels observed.

Soil.--Qualitative analysis of soil samples near Velsicol Chemical Corp. was performed on two samples. The findings are presented in Table 6.22.

Analysis of soil samples was by GLC/MS/COMP according to the protocol in Appendix A. The results are given in Table 6.23. Soil sample P1/C1/L3 was further analyzed in the full scan mode. The results of the spectral interpretation are given in Table 6.24. Spectra of three peaks are included as Figures 6.13, 6.14, 6.15, and 6.16 along with the spectra of standards

Table 6.21. RESULTS OF ANALYSIS OF SEDIMENT AND WATER SAMPLES FOR SEMI-VOLATILE BROMINATED ORGANICS - VELSICOL, INC., EL DORADO, ARKANSAS

Period/Cycle/Location[a]	Sample Type	Tetrabromo-bisphenol A[b] µg/kg	Firemaster 680[c] µg/kg	Tris(2,3-dibromo-propyl)phosphate µg/kg
P1/C1/L1	SD/HHC	30[d]	466[e]	ND[f] 2600[g]
	W/HHC			ND[g]
P1/C1/L3	SD/HHC	ND[f]	ND[f]	ND[f]
	W/HHC			10[g]
P4/C1/L5	SD/HHC	ND[f]	10[h]	ND[f,g]
	W/HHC			2[g]

[a] See Table 6.13 and Figures 6.7 and 6.8.

[b] 2,2'-Bis(dibromo-4-hydroxyphenyl)propane.

[c] 1,2-bis(2,4,6-tribromophenoxy)ethane.

[d] Quantitation by gas chromatography-mass spectrometry with multiple ion detection. The ions 529 and 531 were monitored giving an intensity ratio of 1.57 for the sample compared to 1.5 ± 0.1 for standards under the same conditions.

[e] Quantitation by gas chromatography-mass spectrometry with multiple ion detection. The ion 357 and retention time were used for identification. This ion is not very specific; however, it is the most prominent in the mass spectrum of Firemaster 680.

[f] Not detected by gas chromatography-mass spectrometry with multiple ion detection.

[g] Quantitation by gas chromatography-electron capture detection.

[h] Quantitation by gas chromatography-mass spectrometry with multiple ion detection using three ions, m/e 690 and 688 which are very specific for Firemaster 680 although less sensitive than m/e 357.

Table 6.22. QUALITATIVE ANALYSIS OF VOLATILE HALOGENATED ORGANICS IN SOIL SAMPLES COLLECTED NEAR VELSICOL CHEMICAL CORPORATION, EL DORADO, AK

Period/Cycle/Location	Halogenated Compounds Identified
P1/C1/L2	bromobenzene 1-chloro-2,3-dibromopropane[a] 1,2-dichloroethane
P1/C1/L3	None detected

[a] Tentative identification

Table 6.23. RESULTS OF ANALYSIS OF SOIL SAMPLES FOR SEMI-VOLATILE BROMINATED ORGANICS - VELSICOL, INC., EL DORADO, ARKANSAS

Period/Cycle/Location[a]	Tetrabromo-bisphenol A[b] µg/Kg	Firemaster 680[c] µg/Kg	Tris(2,3-dibromo-propyl)phosphate µg/Kg
P1/C1/L2	ND	5900[d] 6400[e]	ND[k,i]
P1/C1/L3	130[f] 90[h]	400[d] 330[h]	100 - 500[g] 1300[i,j]
P1/C1/L5	ND	ND	ND[k] 300[i]
P1/C1/L7	60[f]	<6	ND[k,i]
P1/C1/L9	ND	166[d]	ND[k,i]
P1/C1/L10	118[f]	253[d]	ND[k,i] 840[i,j]
P1/C1/L13	ND	68[d]	ND[k,i]
P2/C1/L14	ND	100[d]	ND[k,i]

---

[a] See Table 1 and Figures 2 and 3 for location of samples.

[b] 2,2-Bis(dibromo-4-hydroxyphenyl)propane.

[c] 1,2-Bis(2,4,6-tribromophenoxy)ethane.

[d] This compound was quantitated by gas chromatography-mass spectrometry with multiple ion detection. Rentention time and the m/e 357 ion was used. Note should be made that this is not a particularly specific ion and may be subject to some interference.

[e] Quantitation by thin-layer chromatography - scanning spectro-densitometry.

[f] Quantitation is based on two ions, m/e 529 and 531 in the proper intensity ratio of 1.5 ± 0.1 (529/531).

[g] Quantitation and verification was attempted by gas chromatography-mass spectrometry with multiple ion detection. Three of the most prominent ions were used, m/e 419, 417 and 337. The standards gave ion intensities ratios of 0.8 ± 0.2; 1.0; 1.9 ± 0.2, respectively, compared to the sample intensity ratios of 0.4; 1.0; 3.8. This is not very good agreement and indicates further sample purification would be required for a rigorous confirmation.

[h] Confirmed by full scan gas chromatography-mass spectrometry. Additional ions were used for the quantitation of Firemaster 680 (m/e, 688 and 690).

[i] Quantitation by gas chromatography-electron capture.

[j] An attempt to gain additional confirmation by thin-layer chromatography with fluorescein indicator for bromine containing compounds indicated many bromocompounds. There were so many different compounds that no conclusions concerning TRIS could be made.

[k] Not detected by gas chromatography-mass spectrometry with multiple ion detection (< ∿ 5000 µg/Kg).

Table 6.24. BROMINATED COMPOUNDS IDENTIFIED FROM GAS CHROMATOGRAPHY - MASS SPECTROMETRY ANALYSIS OF SOIL SAMPLE P1/C1/L3[a] FROM VELSICOL, INC., EL DORADO, ARKANSAS

Retention[b] Time (min)	Compound
0.19	$C_{12}H_6Br_2O$ (tent.)
0.33	[m/e 360, 362; Br = 3]
0.39	$C_6H_2Br_4$ (tent.) and $C_9H_{14}O_4P\ Br_3$ (tent.)
2.06	$C_{15}H_{12}O_2\ Br_4$[2,2-Bis(dibromo-4-hydroxyphenyl)propane] $C_9H_{15}O_4P\ Br_6$[Tris(2,3-dibromopropyl)phosphate]
3.33	$C_{14}H_8O_2Br_6$[1,2-bis(2,4,6-tribromophenoxy)ethane]
6.06	$C_{12}H_5Br_5O$ (tent.)[c] and $C_{12}H_5Br_5$ (tent.)[c]
6.59	[m/e 690 ± 1, 576 ± 1 and 439 ± 1 containing halogens]
6.86	[m/e 626 ± 1, 609 ± 1, 594 ± 1, 576 ± 1, 429 ± 1 and 339 ± 1 containing halogens]
7.06	$C_{12}Br_{10}O$ [decabromobiphenyl ether]

---

[a] See Table 6.14 and Figures 6.8 and 6.9 for sample location.

[b] Gas chromatography conditions: 2% OV-101 on Gas Chrom Q; column, 45 cm x 0.2 cm i.d.; 20 cc/min helium; initial temperature 220°C, programmed at 12°/min to 300°C.

[c] The identification represents the empirical formula for the highest mass observed in the mass spectrum; however, the higher brominated homologs in this series also give these ions. The retention time is similar to that of the octa- or nona- brominated biphenyl or biphenyl ether.

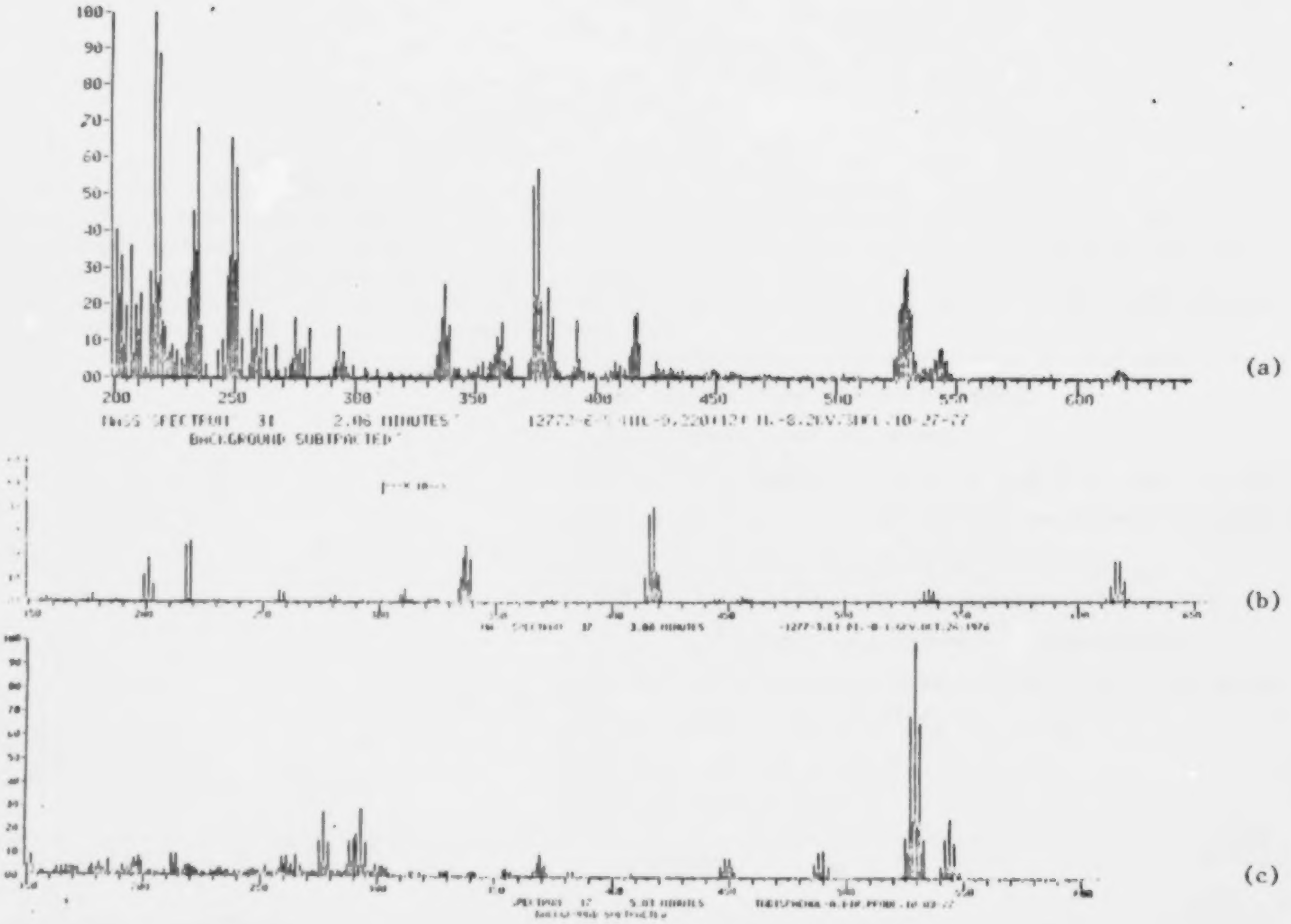


Figure 6.13. Mass spectrum of GC peak eluting at 2.06 min from soil sample L1/C1/L3. (a) Sample spectrum (GLC); (b) TRIS spectrum (Direct probe); (c) Tetrabrom spectrum (Direct probe).

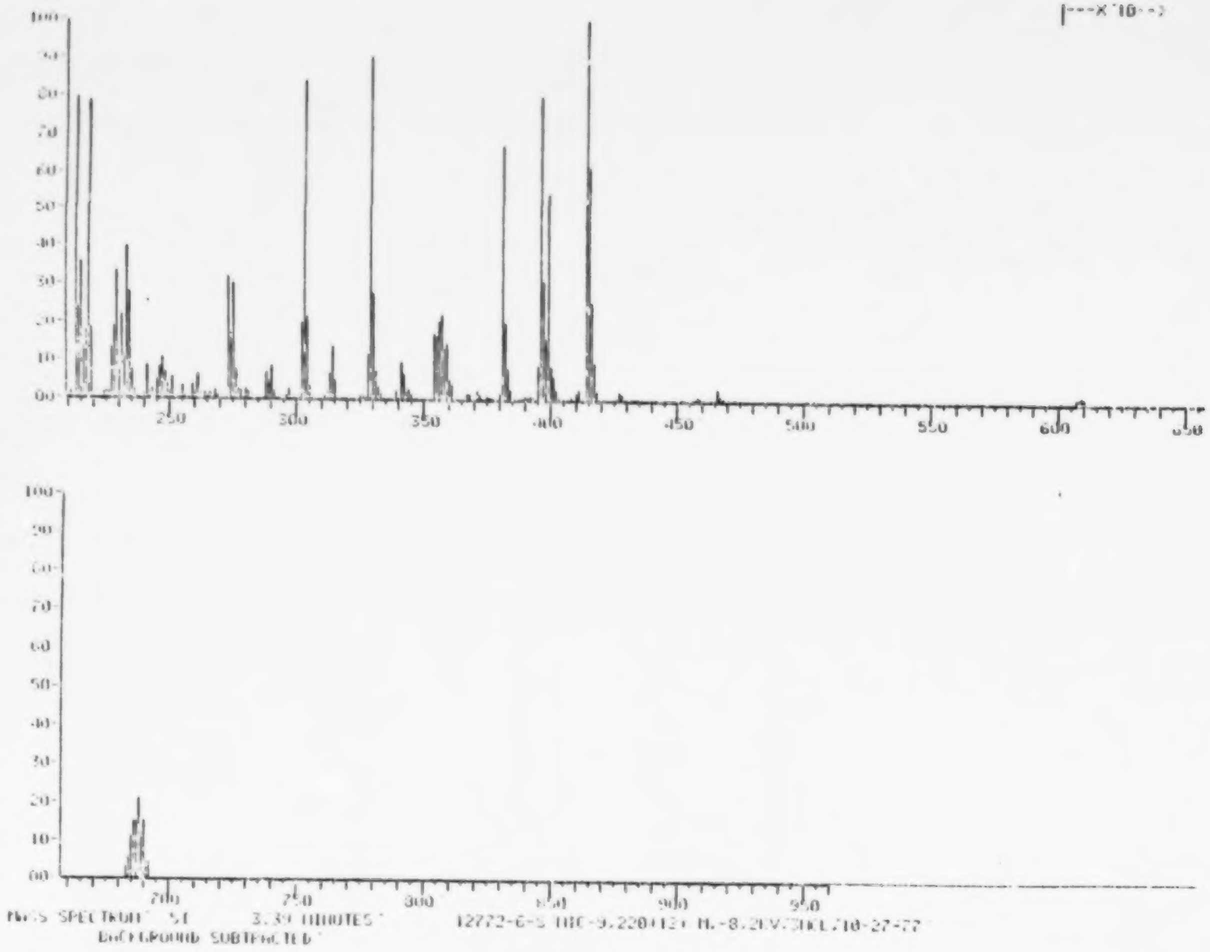


Figure 6.14. Mass spectrum of GC peak eluting at 3.4 min from soil sample P1/C1/L3.

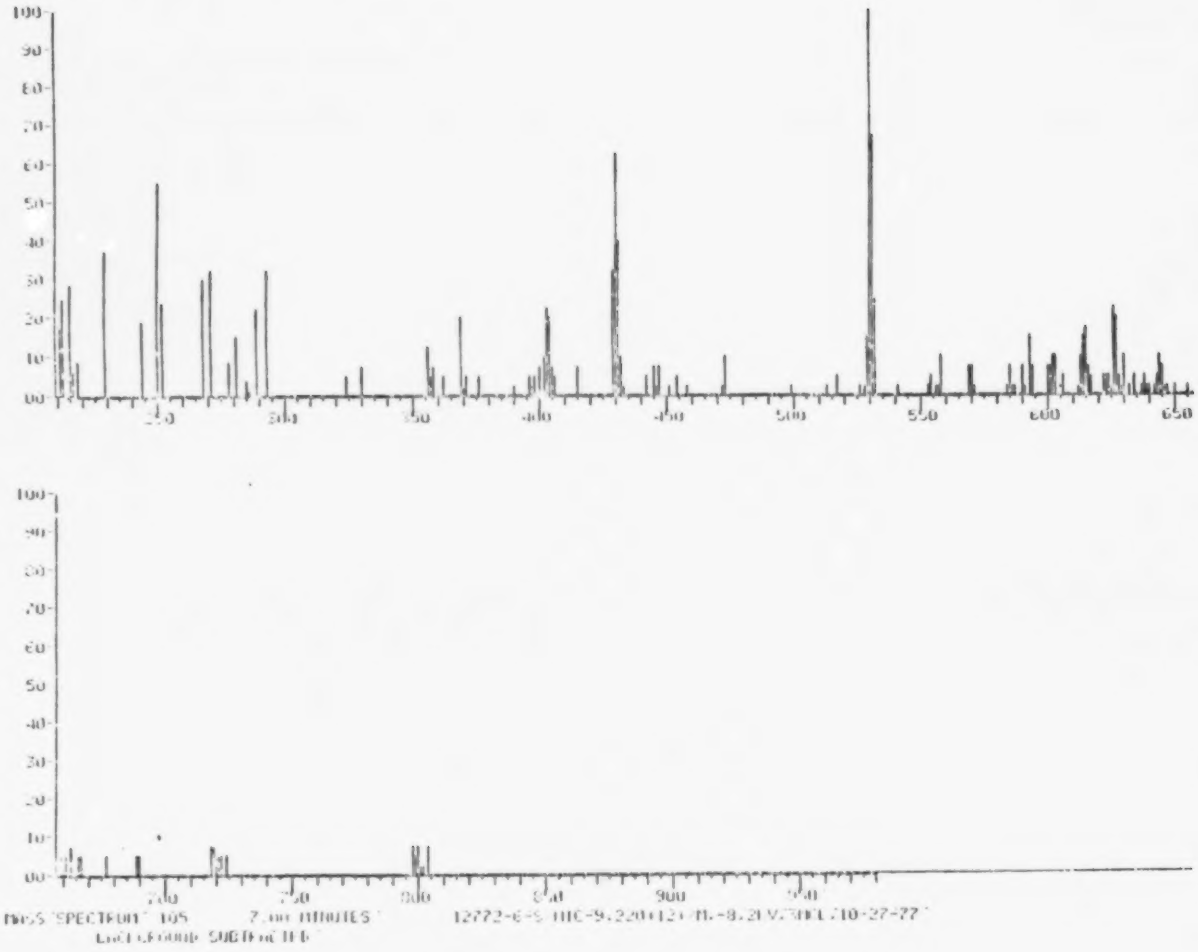


Figure 6.15. Mass spectrum of GC peak eluting at 7.00 min from soil sample P1/C1/L3 identified as decabrom•biphenyl ether.

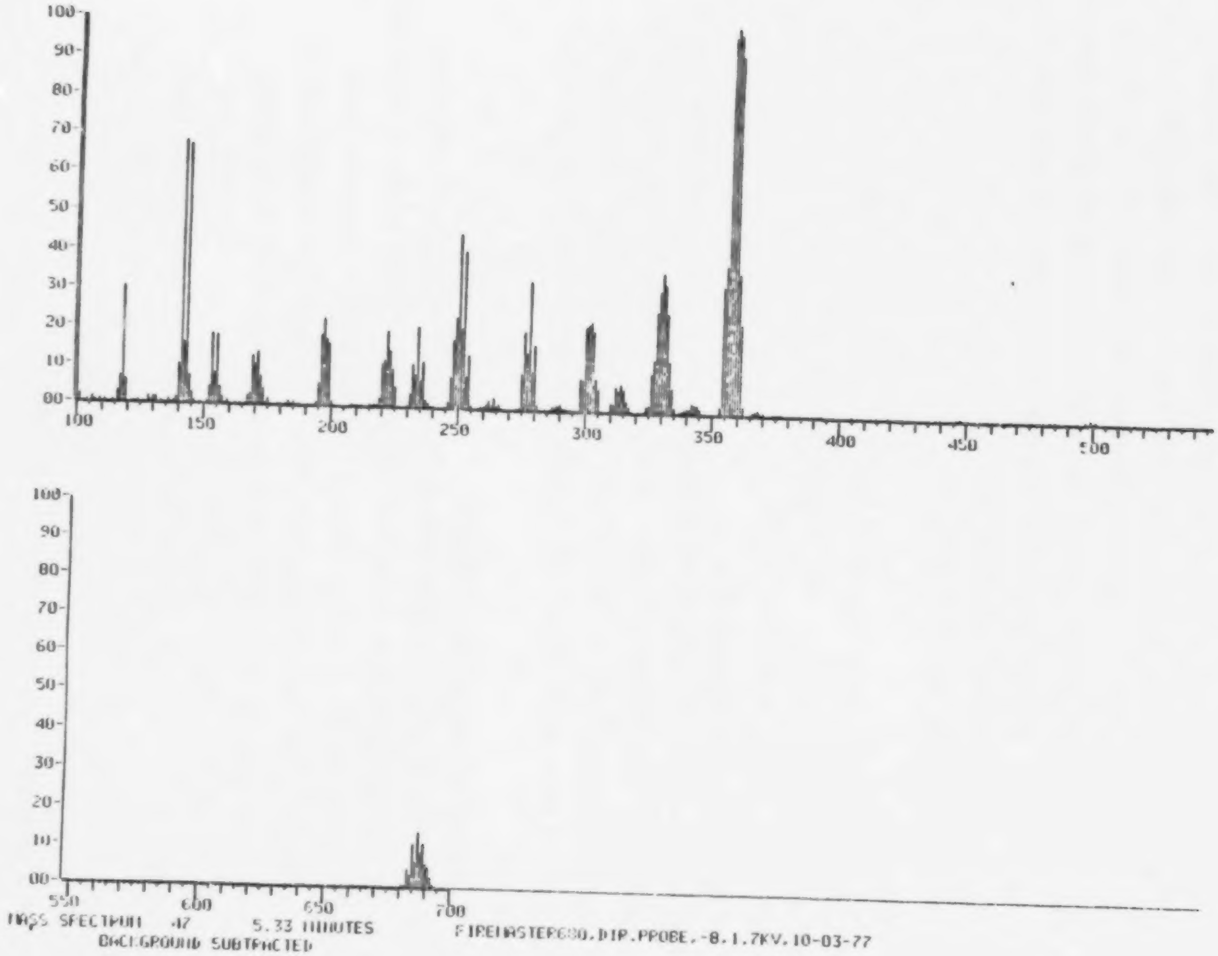


Figure 6.16. Mass spectrum of authentic Firemaster 680 (direct probe).

of the brominated compounds identified. This is the first occasion where TRIS could be confirmed by full scan rather than ion intensity ratios.

Soil sample Pl/Cl/L2 and Pl/Cl/L3 represent contamination by facility activities such as loading and processing the materials found. The samples at locations 5, 7 and 9, although within the facility, are not in areas obviously involved in processing or handling brominated compounds. Locations 10 and 14 are even more remote from the process area and there is no obvious activity which should lead to contamination except for airborne dispersion. (The watershed drains the opposite direction.)

6.2.3 Ethyl Corporation and Vicinity

6.2.3.1 Sampling

Table 6.25 presents the sampling protocol for ambient air surrounding Ethyl Corporation in Magnolia, AK. The corresponding air sampling locations for these periods are given in Figure 6.17.

6.2.3.2 Inorganics in Ambient Air

Table 6.26 presents the halides and halogens which were quantified in ambient air surrouding Ethyl Corporation. Relative to other bromine industrial units, the concentrations of halide and halogen which were detected at Ethyl Corporation were much lower and nearer the detection limit of the analytical methods.

6.2.3.3 Brominated and Other Organics

Air.--The ambient air levels for several volatile brominated organics surrounding Ethyl Corporation are given in Table 6.27. Only three brominated organics, ethylene dibromide, a bromopropane and 1-chloro-3-bromopropane were detected. The highest concentrations observed were for 1,2-dibromoethane which was generally at levels of 1-5 $\mu g/m^3$. No other brominated organics were detected in ambient air (Table 6.27).

Table 6.28 gives the concentrations of ethylene in ambient air that were detected at Ethyl Corporation. Except for Location 1 (9.8 ppm), the concentrations of ethylene were near background levels.

Soil.--No brominated organics were detected.

Table 6.25. AMBIENT AIR SAMPLING PROTOCOL SURROUNDING ETHYL CORP., MAGNOLIA, AK

Period	Cycle	Location	Sampling Time	Sampling Volume (ℓ)	Type of Sample	Meteorological Conditions			
						T(°C)	%RH	Wind Direction Speed (kmph)	Other
P1 (7/26/77)	C1	L1	1620-0935 (7/27/77	99	HHC^{ab}	17-33	50-90	N,NE/6-10	
		L2	1655-1000 (7/27/77)	126	HHC^{ab}				
		L3	1708-1018 (7/27/77)	79	HHC^{ab}				
P2 (7/27/77)	C1	L1	0945-0845 (7/28/77)	120	HHC^{ab}	19-32	65-90	E/5-6 (2 1/2 hrs)	
		L2	1005-0900 (7/28/77)	184	HHC^{ab}			N/7-20 (2 hrs.)	
		L3	1020-1000 (7/28/77)	113	HHC^{ab}			E to N shifting/4-6 (5 hrs)	
		L4	1055-1012 (7/28/77)	∿ 40	HHC^{ab}			N, NW/1-3 (12 1/2 hrs)	pump not fully functional
		L1	0945-1400	181	CBD,CBN^{c}				
		L2	1005-1405	311	CBD,CBN^{c}	19-34	65-92	E/5-6 (2 1/2 hrs)	
		L3	1020-1410	200	CBD,CBN^{c}			N/7-20 (2 hrs)	
		L4	1045-1415	175	CBD,CBN^{c}				
		L1	0940	0.5	VAC				
		L2	1000	0.5	VAC				
		L3	1022	0.5	VAC				
		L4	1040	0.5	VAC				
		L5	1300	0.5	VAC				
		L1	0940-0850 (7/28/77)	1,475,000	Hi-Vol				
		L2	1002-0900 (7/28/77)	2,187,000	Hi-Vol				
P3 (7/28/77)	C1	L1	0850-0845 (7/29/77)	70	HHC^{ab}	22-32	68-92	SE to W/4-5 (4 hrs)	
		L2	0915-0915 (7/29/77)	177	HHC^{ab}			E to W/8-10 (7 hrs)	
		L3	1002-1005 (7/29/77)	118	HHC^{ab}			N, calm (7 hrs) with intermittant NE/5 (1 hr) and SE/8 (1 hr) SE/5 (2 hrs)	
		L4	1035-0955 (7/29/77)	∿210	HHC^{ad}				battery dead at end of period
		L1	0845-1245	167	CBD,CBN^{c}				
		L2	0930-1245	178	CBD,CBN^{c}				
		L3	0955-1420	225	CBD,CBN^{c}				
		L4	1010-1455	171	CBD,CBN^{c}				
		L1	0845	0.5	VAC				
		L2	0900	0.5	VAC				
		L3	0955	0.5	VAC				
		L4	1010	0.5	VAC				near tank car marked allyl chloride
		L6	1050	0.5	VAC				
		L1	0855-0855 (7/29/77)	1,467,000	Hi-Vol				
		L2	1247-0905 (7/29/77)	1,792,000	Hi-Vol				

(continued)

Table 6.25 (cont'd)

Period	Cycle	Location	Sampling Time	Sampling Volume (ℓ)	Type of Sample	T(°C)	Meteorological Conditions		
							%RH	Wind Direction Speed (kmph)	Other
P4 (7/29/77)	C1	L1	0900-1125 (7/30/77)	126	HHC[ab]	19-32	60-92	SW to W/9-12 (9 hrs) mostly calm (11 hrs) with occasional gust (S and SE at 3-5) S/4-15 (5 hrs)	
		L2	0925-1130 (7/30/77)	192	HHC[ab]				
		L3	1015-1150 (7/30/77)	118	HHC[ab]				
		L4	1000-1150 (7/30/77)	<418	HHC[ad]				pump stopped
		L1	0900-1315	170	CBD,CBN[c]			SW to W/9-12	upset at 0915, orange clouds moving toward location 1
		L2	0930-1350	187	CBD,CBN[c]				
		L3	0830-1245	171	CBD,CBN[c]				
		L4	0950-1405	177	CBD,CBN[c]				
		L1	1340	0.5	VAC				
		L2	1350	0.5	VAC				
		L3	1415	0.5	VAC				
		L4	1405	0.5	VAC				
		L1	0900-1245 (7/30/77)	1,673,000	Hi-Vol				
		L2	0910-1205 (7/30/77)	2,331,000	Hi-Vol				

---

[a] DuPont sampler 3-6 ft elevation

[b] Overnight sampling

[c] Nutech Model 220 sampler 3-6 ft elevation

[d] A field adapted Walker Minnow aeration pump.

Locations shown in Figure 6.17.

Key to Sample Type:

HHC - Halogenated Hydrocarbon
CBN - Bromine and Chlorine
CBD - Bromide and Chloride
VAC - Aluminum Vacuum Can

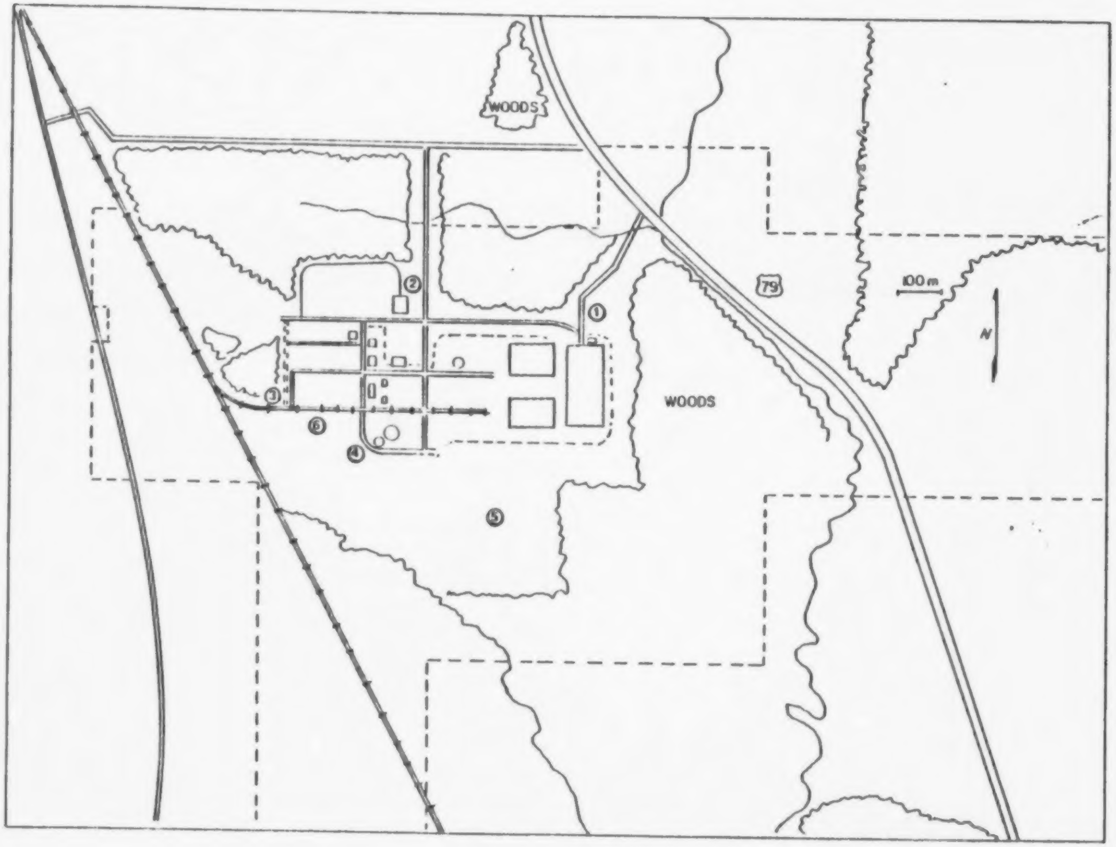

WOODS
79
100 m
N
WOODS
①
②
③
④
⑤
⑥

Figure 6.17. Schematic map of Ethyl Corporation, Magnolia, AK - Air sampling locations P1-P6 (7/26/77 through 7/30/77).

Table 6.26. HALIDES AND HALOGENS QUANTITATED IN AMBIENT AIR SURROUNDING ETHYL CORPORATION, MAGNOLIA, AK[a]

Period/Cycle/Location	Halide as Cl^{-}[b] $\mu g/m^3$	Halogen as Cl_2[b] $\mu g/m^3$
P2/C1/L1	<14	<22
L2	18 ± 12	19 ± 6
L3	<17	<20
L4	39 ± 20	<22
P3/C1/L1	36 ± 12	96 ± 36
L2	45 ± 23	34 ± 23
L4	<12	46 ± 23
P4/C1/L1	57 ± 23	45 ± 11
L2	<20	40 ± 20
L4	41 ± 51	45 ± 22

[a] Refer to Table 6.25 for sampling protocol.

[b] Values are expressed as Cl^{-} or Cl_2; however, if Br^{-} or Br_2 is the predominant species, the values should be multiplied by 1.5.

Table 6.27. AMBIENT AIR LEVELS FOR SEVERAL VOLATILE BROMINATED ORGANICS SURROUNDING ETHYL CORP., MAGNOLIA, AK

Period/Cycle/Location	1,2-Dibromoethane	1-Chloro-3-bromo-propane	Bromopropanes	Bromobenzene	1-Chloro-2-bromo-ethane	Dibromochloro-propanes	Bromoform	Bromodichloro-methane	Allyl bromide	Dibromopropanes	Chlorodibromo-methane	Dibromomethane
P1/C1/L1	ND	T	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
L2	2,957	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
L3	216	39	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
P2/C1/L1	818	482	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
L2	1,008	64	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
L3	1,411	241	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
L4	2,520	678	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
P3/C1/L1	1,638	36	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
L2	1,868	14	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
L3	26	T	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
L4	5,012	T	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
P4/C1/L1	3,791	1,688	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
L2	2,800	20	734	ND	ND	ND	ND	ND	ND	ND	ND	ND
L3	356	ND	T	ND	ND	ND	ND	ND	ND	ND	ND	ND
L4	2,366	171	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table 6.28. CONCENTRATIONS OF ETHYLENE IN AMBIENT AIR SURROUNDING ETHYL CORPORATION, MAGNOLIA, AK

Period/Cycle/Location	ppm Ethylene
P3/C1/L1	9.8
P3/C1/L2	2.9
P3/C1/L3	3.5
P3/C1/L4	3.4
P3/C1/L6	2.1
Lab-1[a]	0.1
Lab-2[a]	2.2
Field-1[b]	0.3
Field-2[b]	0.9
Field-3[b]	0.4
Lab-1[a,c]	3.8
Lab-2[a,d]	10.1
Field-1[b,c]	1.7
Field-2[b,c]	4.9
Field-3[b,d]	6.5
Field-4[b,d]	10.0

[a] Stored at 4°C in the laboratory.

[b] Transported to the sampling area and returned to the lab.

[c] Spiked with 0.9 ppm ethylene.

[d] Spiked with 9.7 ppm ethylene.

6.2.4 Dow Chemical Company and Vicinity

6.2.4.1 Sampling

Table 6.29 gives the ambient air sampling protocol for Dow Chemical Company. Figures 6.18-6.20 depict the air sampling locations described in Table 6.29. Table 6.30 presents the sampling protocols for water and sediment for this area. Figure 6.21 depicts the sampling locations for water and sediment on and in the vicinity of Dow Chemical Co. in Magnolia. Table 6.31 lists the sampling protocols for soil and the locations are given in Figure 6.22.

6.2.4.2 Inorganics in Ambient Air

The concentrations of halides and halogens determined in ambient air surrounding Dow Chemical Co. is given in Table 6.32. No halide was detected in any of these samples with a detection limit of $\sim 5\ \mu g/m^3$. Relatively low concentrations of halogen were detected in samples at locations 3 and 4 during cycles 1 and 2.

6.2.4.3 Brominated and Other Organics

Air.--Table 6.33 presents the concentrations of volatile brominated organics which were estimated in ambient air surrounding Dow Chemical Co. The most prevalent brominated species was 1,2-dibromoethane and the highest concentration observed was 62,848 ng/m^3 during the second sampling period at location No. 4. Included are the concentrations of styrene which were detected in the air samples taken at Dow Chemical Co. The most prevalent occurrence of styrene was observed at L2 during the third sampling period at which time it reached a level of 19,656 ng/m^3.

Table 6.34 presents the concentrations of ethylene in ambient air surrounding Dow. As indicated in this table, the levels of ethylene were generally near background concentrations.

Water and Sediment.--Water and sediment samples were analyzed by the VOA procedure given in Appendix A. The results are presented in Table 6.35. Among the sediment and water samples, P3/C1/L7 contained an extensive number of halogenated organics. These samples were taken in an area subject to overflow runoff from the settling ponds nearby.

Soil.--Soil samples were analyzed by the VOA procedure in Appendix A for the identification of halogenated organics. The results are given in Table 6.36.

Table 6.29. AMBIENT AIR SAMPLING PROTOCOL FOR DOW CHEMICAL CO., MAGNOLIA, AK

Period	Cycle	Location	Sampling Time	Sampling Volume (ℓ)	Type of Sample	T(°C)	Meteorological Conditions		
							%RH	Wind Direction Speed (kmph)	Other
8/1/77 P1	C1	L1	1055-0950 (8/2/77)	169	HHC[ab]	17-32	70-90	N,NE,NW,/2-7	
		L2	1130-1030 (8/2/77)	89	HHC[ab]				
		L3	1208-1100 (8/2/77)	169	HHC[ab]				
		L1	1045-1510	198	CBN,CBD[c]				
		L3	1200-1535	168	CBN,CBD[c]				
		L4	1150-1530	161	CBN,CBD[c]	30-32	70	N,NW/5-7	
		L1	1045-1000 (8/2/77)	1,520,000	Hi-Vol[b]				
		L4	1210-1155 (8/2/77)	1,996,000	Hi-Vol[b]				
8/2/77 P2	C1	L1	1000-1005 (8/3/77)	130	HHC[ab]	14-33	55-92	NE,NW/2-9	
		L2	1040-1025 (8/3/77)	77	HHC[ab]				
		L3	1150-1105 (8/3/77)	729	HHC[cb]				
		L4	1110-1045 (8/3/77)	75	HHC[ab]				
		L5	1230-0945 (8/3/77)	670	HHC[cb]				
		L1	1015-1440	223	CBN,CBD[c]	27-33	60-80	NE/9	
		L3	1155-1450	183	CBN,CBD[c]				
		L4	1115-1455	169	CBN,CBD[c]				
		L5	0955-1355	183	CBN,CBD[c]				
		L3	1100-1040 (8/3/77)	1,950,000	Hi-Vol[b]				
		L5	1005-0950 (8/3/77)	1,472,000	Hi-Vol[b]				
		L1	1020	-	VAC				
		L2	1030	-	VAC				
		L3	1230	-	VAC				
		L4	1200	-	VAC				
		L5	1400	-	VAC				

[ab] DuPont sampler 3-6 ft elevation
[b] Overnight sampling
[c] Nutech Model 220 sampler 3-6 ft elevation

Locations shown in Figures 6.18-6.20

Key to Sample Type:
HHC - Halogenated Hydrocarbon
CBN - Bromine and chlorine
CBD - Bromide and Chloride
VAC - Aluminum Vacuum Can

(continued)

Table 6.29 (cont'd)

Period	Cycle	Location	Sampling Time	Sampling Volume (ℓ)	Type of Sample	T(°C)	Meteorological Conditions		
							%RH	Wind Direction Speed (kmph)	Other
8/3/77 P3	C1	L1	1015-0830 (8/4/77)	180	HHC^{ab}	16-35	45-92	E Var, NW/2-9	
		L2	1035-0840 (8/4/77)	59	HHC^{ab}				
		L3	1120-0846 (8/4/77)	640	HHC^{bc}				
		L4	1100-0900 (8/4/77)	178	HHC^{ab}				
		L5	1000-0820 (8/4/77)	652	HHC^{bc}				
		L1	1005-1615	302	CBN,CBD^{c}	32-34	48	E Var/5-8	
		L3	1045-1630	280	CBN,CBD^{c}				
		L4	1100-1645	275	CBN,CBD^{c}				Upset of Br_2 during at least the last 1/2 hr. Odor of Br_2
		L5	0950-1600	287	CBN,CBD^{c}				
		L6	1600	-	VAC				
		L3	1050-0850 (8/4/77)	1,793,000	Hi-Vol^{b}				
		L5	1000-0825 (8/4/77)	1,313,000	Hi-Vol^{b}				
	C2	L1	1625-0830 (8/4/77)	506	CBN,CBD^{bc}	16-34	45-92	E/3-5 (4 hrs.)	Upset of Br_2 just before Sampling
		L3	1640-0850 (8/4/77)	424	CBN,CBD^{bc}			NW/<2 (12 hrs.)	
		L4	1650-0900 (8/4/77)	518	CBN,CBD^{bc}				Odor noticeable, possibly HBr
		L5	1615-0820 (8/4/77)	392	CBN,CBD^{bc}				

[ab] DuPont sampler 3-6 ft elevation

[b] Overnight sampling

[c] Nutech Model 220 sampler 3-6 ft elevation

Location shown in Figures 6.18-6.20

Key to Sample Type:
HHC - Halogenated Hydrocarbon
CBN - Bromine and chlorine
CBD - Bromide and Chloride
VAC - Aluminum Vacuum Can

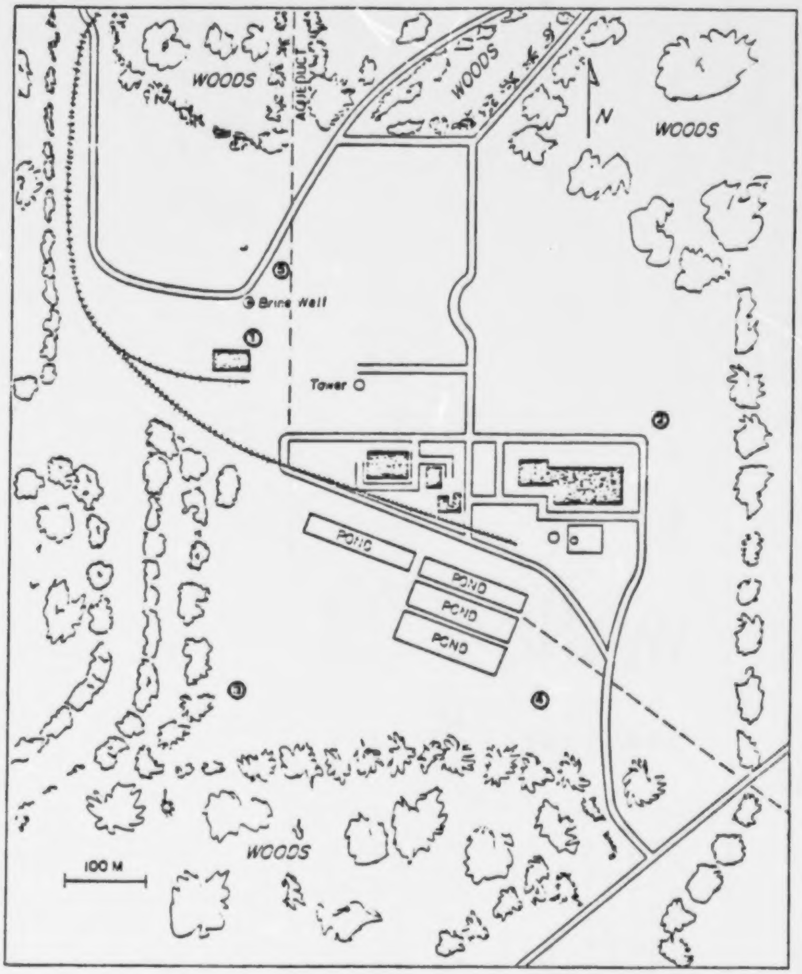

WOODS
AQUEDUCT
WOODS
N
WOODS
⑤
Brine Well
①
Tower
②
POND
POND
POND
POND
③
④
WOODS
100 M

Figure 6.18. Schematic map of Dow Chemical Company, Magnolia, Arkansas - Air sampling locations for P1 - 8/1/77

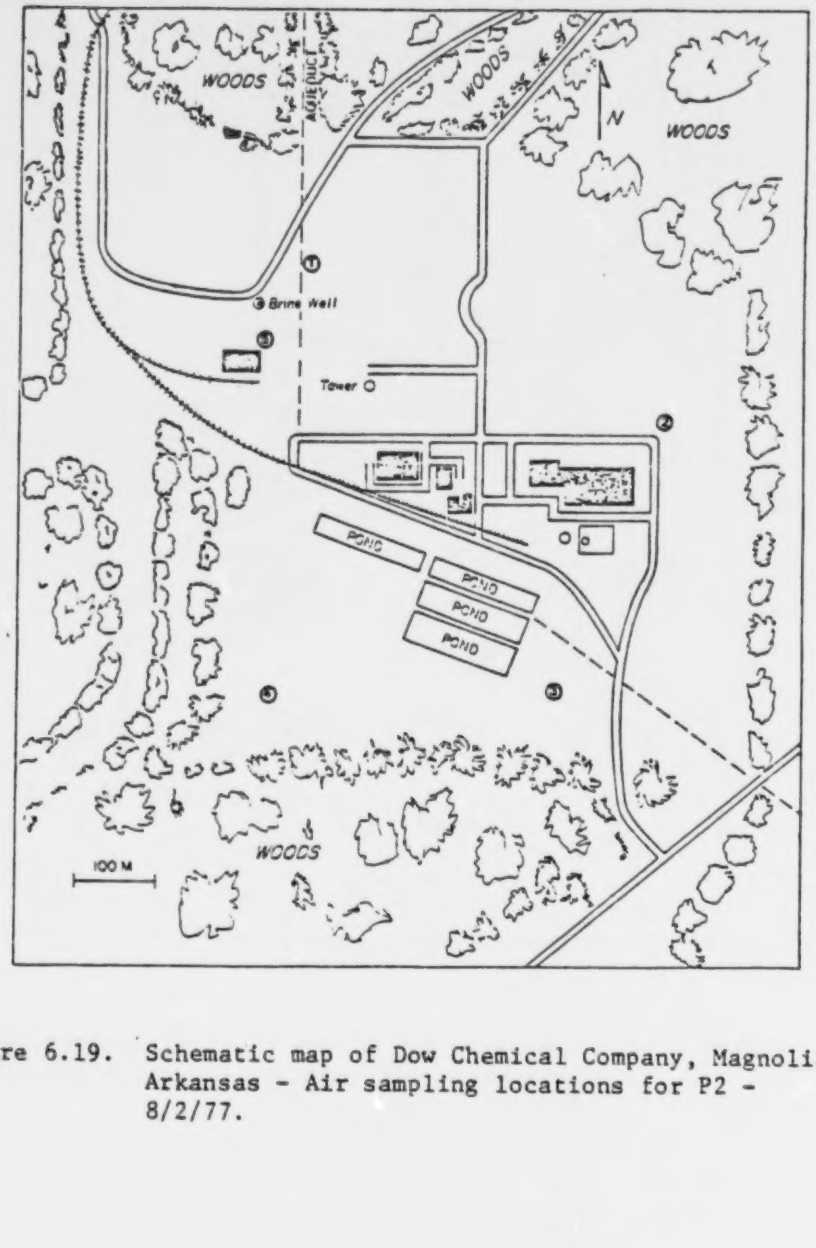

WOODS
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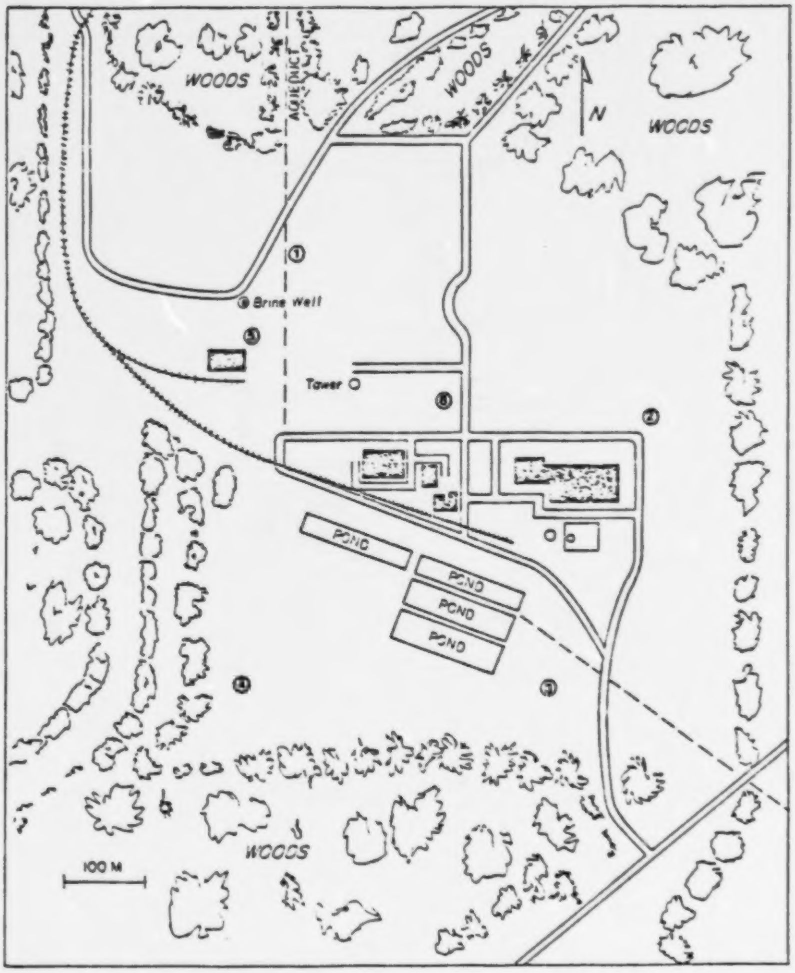
Figure 6.19. Schematic map of Dow Chemical Company, Magnolia, Arkansas - Air sampling locations for P2 - 8/2/77.


WOODS
AQUEDUCT
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Brine Well
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Tower
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POND
POND
POND
POND
④
③
WOODS
100 M

Figure 6.20. Schematic map of Dow Chemical Company, Magnolia, Arkansas - Air sampling locations for P3 - 8/3/77

Table 6.30. WATER AND SEDIMENT SAMPLING PROTOCOLS FOR DOW CHEMICAL COMPANY, MAGNOLIA, ARKANSAS

Period	Cycle	Location	Sample Type	Sample Size	Comments
P1 7/30/77	C1	L1	W/HHC	2ℓ	water from small pond - runoff after rain
		L2	W/HHC	2ℓ	pond water
			SD/HHC	2ℓ	pond sediment (drainage from pond)
		L3	W/HHC	2ℓ	drainage from pond
		L4	W/HHC	2ℓ	stream water
			SD/HHC	2ℓ	stream sediment
P2 8/1/77	C1	L5	W/HHC	2ℓ	runoff (after rain) from Dow settling ponds
		L6	W/HHC	2ℓ	stream water
P3 8/2/77	C1	L7	W/HHC	2ℓ	standing water
			SD/HHC	2ℓ	
		L8	W/HHC	2ℓ	stream water
		L9	W/HHC	2ℓ	small stream
P4 8/3/77	C1	L10	W/HHC	2ℓ	pond beside road
			SD/HHC	2ℓ	pond beside road
		L11	W/HHC	2ℓ	very slow stream

Locations are shown in Figure 6.21.
W = water samples
SD = sediment samples
HHC = for halogenated hydrocarbon analysis

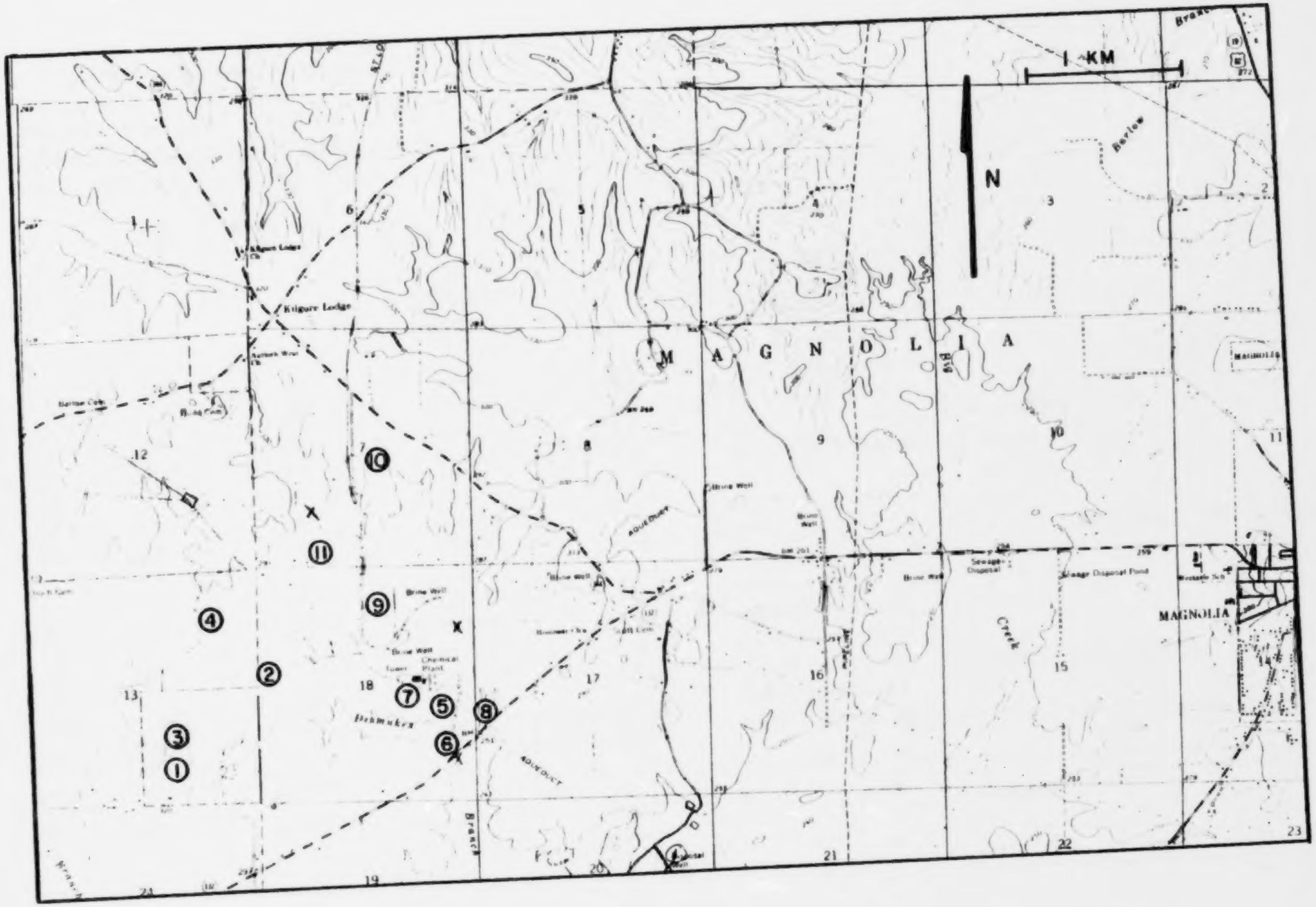
1 KM
N
M A G N O L I A
MAGNOLIA
Kilgore Lodge
Brine Well
Chemical Plant
Creek
Branch
AQUEDUCT
Sewage Disposal Pond
①
②
③
④
⑤
⑥
⑦
⑧
⑨
⑩
⑪

Figure 6.21. Water sampling locations in the vicinity of Dow Chemical Co., Magnolia, Arkansas (7/29/77 - 8/3/77).

Table 6.31. SOIL SAMPLING PROTOCOLS FOR DOW CHEMICAL COMPANY, MAGNOLIA, ARKANSAS[a]

Period	Cycle	Location	Sample Size	Comments
P1 7/30/77	C1	L1	2 cores	
		L2	2 cores	Box Springs Road
P3 8/2/77	C1	L3	2 cores	Near air sampler
		L4	2 cores	Near air sampler
		L5	2 cores	At NE corner of drive into plant
		L6	2 cores	Rt. 344 at Rt. 132

[a] Locations of sampling are shown in Figure 6.22.

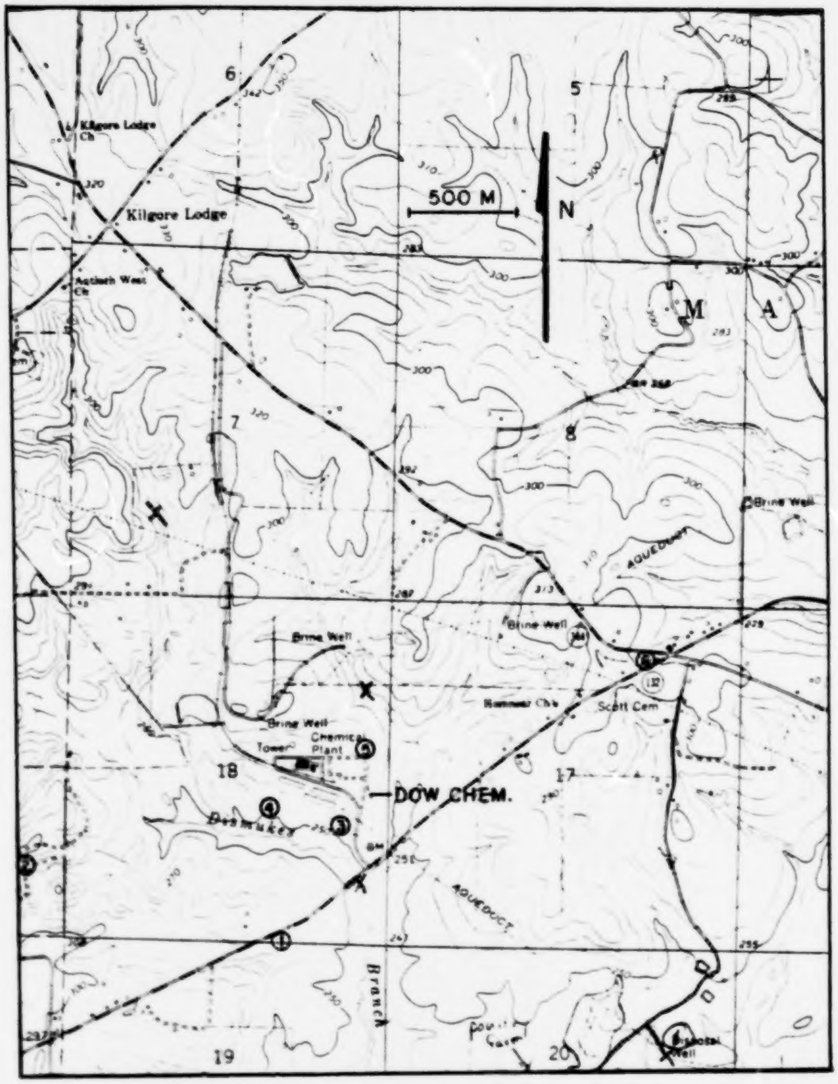
500 M
N
Kilgore Lodge Ch
Kilgore Lodge
Antioch West Ch
M
A
6
5
7
8
18
17
19
20
Brine Well
Brine Well
Brine Well
Brine Well
Tower
Chemical Plant
DOW CHEM.
Scott Cem
AQUEDUCT
AQUEDUCT
Branch
Disposal Well
①
②
③
④
⑤
⑥
300
320
283
250

Figure 6.22. Sampling locations for soil samples collected in the vicinity of Dow Chemical Co. (7/30/77 - 8/2/77).

Table 6.32. HALIDES AND HALOGENS QUANTITATED IN AMBIENT AIR SURROUNDING DOW CHEMICAL COMPANY MAGNOLIA, AK

Period/Cycle/Location[a]	Halide as Cl^-[b] $\mu g/m^3$	Halogen as Cl_2[b] $\mu g/m^3$
P3/C1/L2	< 5	< 12
L3	< 5	64 ± 5
L4	< 6	< 6
P3/C2/L2	< 5	< 10
L3	< 6	14 ± 7
L4	< 4	18 ± 9

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[a] Refer to Table 6.29 for sampling protocol.

[b] Values are expressed as Cl^- or Cl_2; however, if Br^- or Br_2 is the predominant species, the values should be multiplied by 1.5.

Table 6.33. ESTIMATED LEVELS OF VOLATILE BROMINATED ORGANICS IN AMBIENT AIR SURROUNDING DOW CHEMICAL CO., MAGNOLIA, AK[a]

Period/Cycle/Location	Bromobenzene	1-Chloro-2-bromo-ethane	1,2-Dibromoethane	Dibromochloropropane	Bromoform	2-Chloro-3-bromo-propane	Dibromopropane	Dibromochloro-methane	Styrene
P1/C1/L1	ND	ND	62	25	ND	ND	ND	ND	907
L2	ND	ND	462	75	ND	ND	ND	ND	694
L3	ND	445	40,415	1,996	8	ND	ND	ND	12,158
P2/C1/L1	ND	ND	1,509	99	ND	ND	T	ND	1,103
L2	ND	ND	ND	ND	ND	ND	ND	ND	
L3	ND	163	30,156	624	ND	ND	T	ND	10,016
L4	ND	1,089	62,484	6,653	ND	ND	T	ND	15,978
L5	ND	32	14,028	300	ND	ND	T	ND	1,758
P3/C1/L1	ND	ND	179	36	ND	ND	T	ND	960
L2	66	ND	1,744	100	380	ND	ND	ND	19,656
L3	23	304	30,172	795	ND	ND	ND	ND	5,089
L4	140	251	921	188	ND	ND	T	ND	130
L5	35	403	59,438	2,002	50	ND	T	ND	14,272

---

[a] Concentrations are in ng/m^3.

Table 6.34. CONCENTRATIONS OF ETHYLENE IN AMBIENT AIR SURROUNDING DOW CHEMICAL CO.

Period/Cycle/Location	ppm Ethylene
P2/C1/L1	1.6
P2/C1/L2	2.4
P2/C1/L3	1.8
P2/C1/L4	2.2
P2/C1/L5	1.9
Lab-1[a]	0.1
Lab-2[a]	2.2
Field-1[b]	0.3
Field-2[b]	0.9
Field-3[b]	0.4
Lab-1[a,c]	3.8
Lab-2[a,d]	10.1
Field-1[b,c]	1.7
Field-2[b,c]	4.9
Field-3[b,d]	6.5
Field-4[b,d]	10.0

[a] Stored at 4°C in the laboratory.

[b] Transported to the sampling area and returned to the lab.

[c] Spiked with 0.9 ppm ethylene.

[d] Spiked with 9.7 ppm ethylene.

Table 6.35. QUALITATIVE ANALYSIS OF WATER AND SEDIMENT SAMPLES COLLECTED NEAR DOW CHEMICAL COMPANY, MAGNOLIA, AK

Period/Cycle/Location	Sample Medium	Halogenated Compounds Identified[a]
P1/C1/L2	water	ND[b]
L4	water	ND
P2/C1/L5	water	tetrachloroethylene
P3/C1/L7	water	bromopropene 1,2-dichloroethane dibromoethene trichloroethene chlorobromoethane 1,2-dibromoethane chlorobutene bromodichloropropane 1-chloro-2,3-dibromopropane
	sediment	bromobenzene bromoform 1,2-dibromoethane 1-chloro-2-bromoethane[c] 1-chloro-2,3-dibromopropane[c] 1,2-dichloroethane[c]
P4/C1/L11	water	1,2-dichloroethane[c]

---

[a] Analysis by VOA method with GC/MS/COMP detection.

[b] None detected.

[c] Tentative identification.

Table 6.36. QUALITATIVE ANALYSIS OF SOIL SAMPLES COLLECTED NEAR DOW CHEMICAL COMPANY, MAGNOLIA, AK

Period/Cycle/Location	Halogenated Compounds Identified[a]
P1/C1/L1	ND[b]
L2	1,2-dichloroethane
P3/C1/L3	chloroform
L4	ND
L5	1,2-dichloroethane[c]
L6	ND

[a] Analysis by VOA method with GC/MS/COMP detection.

[b] None detected.

[c] Tentative identification.

6.2.5 Samples from Human Population

6.2.5.1 Sampling

Samples of human hair were obtained from El Dorado and Magnolia barber shops (Table 6.37). In order to obtain enough material for analysis, composite samples were made.

In conjunction with a local pediatrician (Dr. James Sykes), human placenta and cord were obtained from six deliveries in El Dorado, AK during the period of July 22 to August 5, 1977.

6.2.5.2 Brominated Organics

Composites of human hair from each of the barber shops were analyzed as three separate samples (Table 6.38). Two of the three composites had detectable quantities of Decarbrom. Since the three composites surveyed a total of ~40 individuals, these findings mean that a minimum of 5% (2 out of 40) of the population had detectable levels of Decabrom. Tetrabrom was confirmed in one sample but interferences prevented confirmation in either of the other two composites.

Eight of the placenta samples were extracted and four were submitted to GC/MS/COMP analysis. The level of background was so high that mg/kg concentrations would have had to be present for detection. No brominated compounds could be identified in these samples. Further purification would no doubt improve the sensitivity of the analysis.

6.3 QUALITY ASSURANCE

The validity of the data generated under this task depended directly upon the quality of the analytical procedures. As such, a strict quality assurance program was established as discussed below. The heart of the quality assurance program was the division of the task into subtasks which focused upon the medium or analysis to be performed. Each subtask had a leader who was responsible for its execution including method validation, sampling, sample analysis, quality control, and data interpretation. The definite delineation of responsibilities reduced the chances of error through poor communication.

6.3.1 Analytical Protocol Validation

Depending on the exact nature of the analytical scheme, each step of a protocol was validated through the use of blanks and spiked samples. The

Table 6.37. SAMPLING PROTOCOL FOR SAMPLES OF THE HUMAN POPULATION

Period	Cycle	Location	Site	Sample Type	Comments
P1 7/23/77	C1	L1	El Dorado	Hair	approximately 16 individuals
		L2	El Dorado	Hair	approximately 20 individuals
		L3	El Dorado	Hair	7 individuals
P2 7/27/77	C1	L1	Magnolia	Hair	unknown number of individuals
P3 7/30/77-8/4/77	C1	L1	Union County Hospital El Dorado	Placenta/ Cord	tissue from normal deliveries at the hospital during the period shown
		L2			
		L3			
		L4			
		L5			
		L6			
		L7			
		L8			

Table 6.38. ANALYSIS OF HUMAN HAIR COLLECTED IN EL DORADO, ARKANSAS FOR SEMI-VOLATILE BROMINATED ORGANICS[a]

Period/Cycle/Location	Tetrabromobisphenol A[c] (μg/Kg)	Decabromobiphenyl ether (μg/Kg)
P7/C1/L14	2.0[d]	5[e]
P7/C1/L15	>13[f]	0.3[g]
P7/C1/L16	>0.7[f]	ND[h]

[a] Quantitation by gas chromatography/mass spectrometry using multiple ion detection.

[b] See Table 6.37 for protocol.

[c] 2,2'-Bis(dibromo-4-hydroxyphenyl)propane.

[d] The two ions, 528 and 530, were observed at the correct gc retention time with the correct intensity ratio, 1.6 *vs*. 1.5 for the standard.

[e] Confirmed by full scan gas chromatography/mass spectrometry.

[f] The two ions, 528 and 530, were observed at the correct gc retention time; however, the ion intensity ratios were 2.3 and 0.94 for P7/C1/L15 and P7/C1/L16, respectively, compared to 1.5 for the standard. These samples would require further purification in order to determine whether tetrabromobisphenol A is or is not present.

[g] Unconfirmed.

[h] Not detected - approximately 0.1 μg/g is required to detect this compound.

validations were conducted using sufficient replication to provide statistically reliable recovery data.

The specific details of the validation experiments and their results are discussed in Section 3.0.

6.3.2 Field Sampling Quality Assurance

6.3.2.1 Quality Control Samples

Blank and spiked samples were created to assure that compounds identified in field samples are not artifacts and to assure that compounds collected in the field are retained in the sample through storage and analysis. For most of the sample matrices, duplicate blank and spiked samples were taken to the field to approximate the conditions to which the samples were subjected. In addition, duplicate blank and control samples remained in the laboratory to monitor storage efficiency and to provide a crosscheck on the field blank and control samples. Blanks and control samples for each medium are summarized in Table 6.39.

6.3.2.2 Sample Identification Protocol

During sample collection, a sample data sheet (Figures 6.23 and 6.24) was maintained for each sample. The sampling locations for each sampling period were recorded on a detailed area map. The coded form contained information such as date and time of sampling, locations, sampling parameters and meteorological information. The alpha-numeric sample code was also fixed directly to the sample container at that time.

Following each day's sample collection, the protocol sheets and sample labels were independently reviewed by two field personnel to assure that all information was logged in, that the codes were self-consistent and that there was no duplication. Upon returning to the laboratory, the samples were again checked for proper labeling.

6.3.2.3 Sample Containers

Sample containers were selected for inertness and ability to maintain sample integrity. Screw caps were lined with foil or teflon and plastic bags were made of Tedlar®. No polyethylene or other standard commercial plastic was allowed to come in contact with the samples. Prior to field sampling, each container was scrupulously cleaned as discussed in Section 3.3.3.1.

Table 6.39. INVENTORY OF CONTROLS AND BLANKS FOR QUALITY ASSURANCE FOR ARKANSAS FIELD SAMPLING - JULY AND AUGUST, 1977

Sample Type	Blanks		Controls		Compound	Concentrations
	Laboratory	Field	Laboratory	Field		
Charcoal cartridges	2	7	2	8	methyl chloride	309 ng
					methyl bromide	100 ng
					vinyl chloride	254 ng
					vinyl bromide	250 ng
Tenax cartridges	2	3	2	4	perfluorobenzene [a]	201 ng
					perfluorotoluene [a]	85 ng
					ethylene dibromide	350 ng
					bromobenzene	250 ng
					1,2-dibromopropane	304 ng
					1-bromo-2-chloroethane	308 ng
					dibromomethane	150 ng
		2		2	perfluorobenzene [a]	250 ng
					perfluorotoluene [a]	105 ng
					dibromomethane	155 ng
					1,2-dibromopropane	314 ng
					1-bromo-2-chloroethane	320 ng
Vacuum cannisters	2	3	3	4	methyl chloride	6, 60 and 300 ppb
					methyl bromide	35, 350 and 1750 ppb
	2	3	2	4	ethylene	0.884 and 9.72 ppm
					ethane	0.880 and 9.69 ppm
Impinger solutions	4	4	8	8	chloride, bromide in deionized water	0.5 and 1.0 ppm each ion
	4	4	8	8	chloride, bromide in alkaline arsenite solution	0.5 and 1.0 ppm each ion

(continued)

Table 6.39 (cont'd)

Sample Type	Blanks		Controls		Compound	Concentrations
	Laboratory	Field	Laboratory	Field		
Glass fiber filters	2	3		2	tetrabromobisphenol A	49, 198, 260, 520 ng/cm^2
					decabromobiphenyl ether	49, 198, 260, 520 ng/cm^2
					tris-(2,3 dibromopropyl) phosphate	101, 202, 540, 1080 ng/cm^2
Water	2^a	3^a	2	4	1-chloro-1-butene	1 and 5 μg/100 ml
					1,2-dichloroethane	1 and 5 μg/100 ml
					1-bromo-2-chloroethane	1 and 5 μg/100 ml
					1,2-dibromoethane	1 and 5 μg/100 ml
					bromobenzene	1 and 5 μg/100 ml
					m-chlorotoluene	1 and 5 μg/100 ml
			2^b	4	tris(2,3-dibromopropyl) phosphate	21 and 210 ppb
					pentabromophenol	9.6 and 95 ppb
					2,4,6-tribromophenol	10.7 and 107 ppb
					tetrabromobisphenol A	9.8 and 100 ppb
					decabromobiphenyl ether	9.6,96 and 105 ppb
					tetrabromophthalic anhydride	10 and 100 ppb
					2,3-dibromopropanol	20 and 200 ppb
					bromobenzene	10.8 and 108 ppb
					1,2-dibromo-3-chloropropane	11.2 and 112 ppb
					hexabromocyclododecane	10 and 100 ppb
					bromoform	12.2 and 122 ppb
					1,2,-dibromoethane	14.5 and 145 ppb
					2,2',4,4',6,6'-hexabromo biphenyl	9.6 and 96 ppb

(continued)

Table 6.39 (cont'd)

Sample Type	Blanks Laboratory	Blanks Field	Controls Laboratory	Controls Field	Compound	Concentrations
Vegetation	2	3	2	4	1-chloro-1-butene	10 and 50 μg/2 g Vegetation
					1,2-dichloroethane	
					1-bromo-2-chloroethane	
					1,2-dibromoethane	
					bromobenzene	
					m-chlorotoluene	
	2	3	2	4	tris(2,3-dibromopropyl) phosphate	21 and 210 ppb
					pentabromophenol	9.6 and 96 ppb
					2,4,6-tribromophenol	10.7 and 107 ppb
					tetrabromobisphenol A	10.0 and 100 ppb
					decabromobiphenyl ether	10.5 and 105 ppb
Milk	2[a]	2[a]	4[c]	2	1-chloro-1-butene [a]	5 μg/100 ml
					1,2-dichloroethane [a]	5 μg/100 ml
					1-bromo-2-chloroethane [a]	5 μg/100 ml
					1,2-dibromoethane a	5 μg/100 ml
					bromobenzene [a]	5 μg/100 ml
					m-chlorotoluene [a]	5 μg/100 ml
					tris(2,3-dibromopropyl) phosphate [b]	42 and 4.2 μg/200 ml
					pentabromophenol [b]	1.9 and 19 μg/200 ml
					2,4,6-tribomophenol [b]	2.1 and 21 μg/200 ml
					tetrabromobisphenol A[b]	2.0 and 20 μg/200 ml
					decabromobiphenyl ether[b]	2.1 and 21 μg/200 ml

(continued)

Table 6.39 (cont'd)

Sample Type	Blanks		Controls		Compound	Concentrations
	Laboratory	Field	Laboratory	Field		
Soil	2	3	2	4	1-chloro-1-butene	10 and 50 μg/20 g soil.
					1,2-dichloroethane	
					1-bromo-2-chloroethane	
					1,2-dibromoethane	
					bromobenzene	
					m-chlorotoluene	
	2	3	2	4	tris(2,3-dibromopropyl) phosphate	21 and 210 ppb
					pentabromophenol	9.6 and 96 ppb
					2,4,6-tribromophenol	10.7 and 107 ppb
					tetrabromobisphenol A	10.0 and 100 ppb
					decabromobiphenyl ether	10.5 and 105 ppb
Sediment	2	3	2	4	1-chloro-1-butene	10 and 50 μg/20 g soil
					1,2-dichloroethane	
					1-bromo-2-chloroethane	
					1,2-dibromoethane	
					bromobenzene	
					m-chlorotoluene	
	2	3	2	4	tris(2,3-dibromopropyl) phosphate	21 and 210 ppb
					pentabromophenol	9.6 and 96 ppb
					2,4,6-tribromophenol	10.7 and 107 ppb
					tetrabromobisphenol A	10.0 and 100 ppb
					decabromobiphenyl ether	10.5 and 105 ppb

(continued)

Table 6.39 (cont'd)

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a Laboratory and field blanks serve for volatile and semi-volatile analysis.

b Two of these contols contained only the first five compounds at the higher concentration.

c Two of these controls contained the first six compounds and two contained the last five compounds.

[illegible] External standard

Abbr. Code: ________________

FIELD SAMPLING PROTOCOL SHEET - B

Date: ______________________________ Medium: _______________( )

(__________) Project No. (_______) Operator (_____) Period (_______________) Medium/Rationale (____) State

Municipality ____( )

Address ____

Site ____( )

Location ____( )

Sample Code ____

Code Key:
W - Water V - Vegetation
S - Soil A - Animal
SD - Sediment M - Miscellaneous
....
G - Grab C - Composited

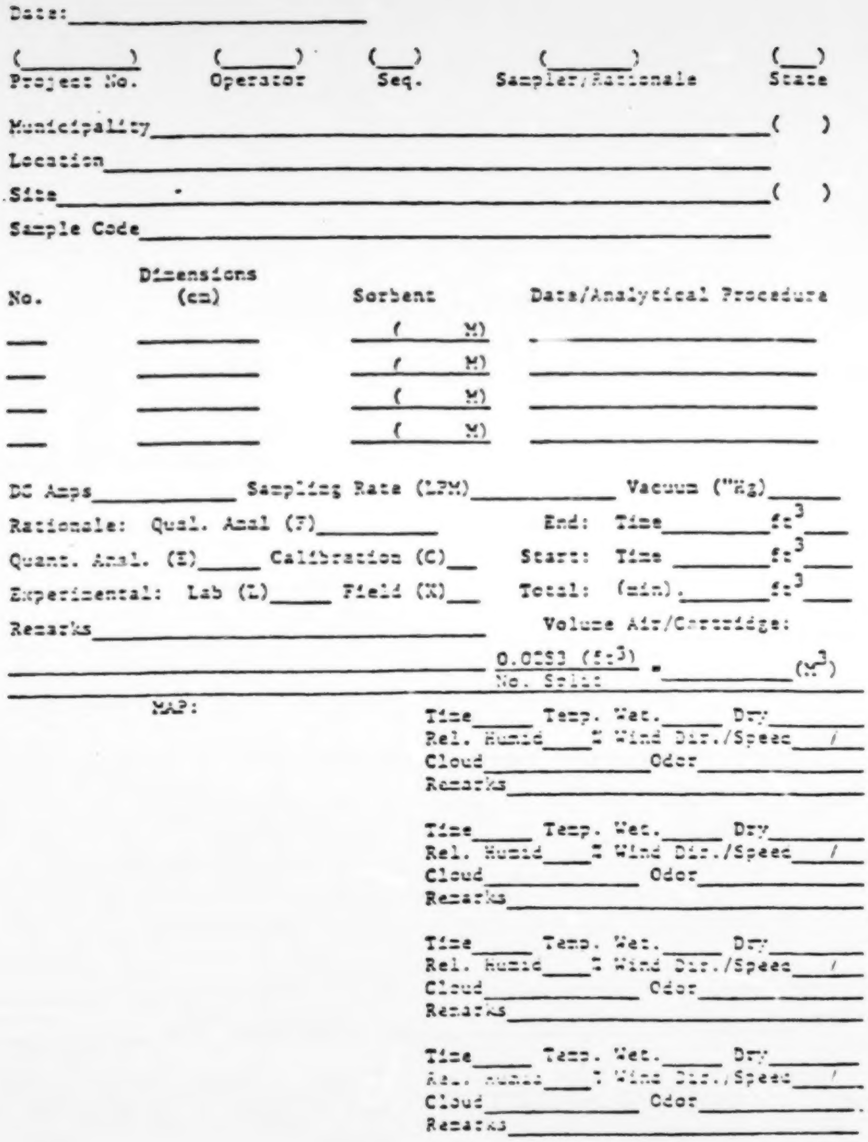
Sample size ____________________ Sampling rate ____________________

Time_____Temp. Wet._____ Dry _________	Time_____Temp. Wet._____Dry _________
Re. Humid_____% Wind Dir./Speed ___/___	Rel. Humid_____% Wind Dir./Speed___/___
Cloud _______________Odor _____________	Cloud _______________Odor _____________
Remarks ______________________________	Remarks ______________________________

End: Time ___________, Date _________
Start: Time ___________, Date _________

Remarks/Map:

Figure 6.23. Field sampling protocol for condensed matrices.



Date: ____________

(________) Project No.
(______) Operator
(__) Seq.
(______) Sampler/Rationale
(__) State

Municipality ______________________ ( )
Location ______________________
Site ______________________ ( )
Sample Code ______________________

No.	Dimensions (cm)	Sorbent	Data/Analytical Procedure
___	________	(M)	____________
___	________	(M)	____________
___	________	(M)	____________
___	________	(M)	____________

DC Amps ________ Sampling Rate (LPM) ________ Vacuum ("Hg) ______
Rationale: Qual. Anal (F) ________
End: Time ________ ft^3 ___
Quant. Anal. (E) _____ Calibration (C) __
Start: Time ________ ft^3 ___
Experimental: Lab (L) _____ Field (X) __
Total: (min). ________ ft^3 ___
Remarks ______________________
Volume Air/Cartridge:

$$\frac{0.0283\ (ft^3)}{\text{No. Split}} = \_\_\_\_\_\_\ (M^3)$$

MAP:

Time _____ Temp. Wet. _____ Dry _____
Rel. Humid ___ % Wind Dir./Speed ___/___
Cloud ________ Odor ________
Remarks ______________________

Time _____ Temp. Wet. _____ Dry _____
Rel. Humid ___ % Wind Dir./Speed ___/___
Cloud ________ Odor ________
Remarks ______________________

Time _____ Temp. Wet. _____ Dry _____
Rel. Humid ___ % Wind Dir./Speed ___/___
Cloud ________ Odor ________
Remarks ______________________

Time _____ Temp. Wet. _____ Dry _____
Rel. Humid ___ % Wind Dir./Speed ___/___
Cloud ________ Odor ________
Remarks ______________________

Figure 6.24. Field sampling protocol for ambient air

6.3.2.4 Sample Storage

At the end of each day's sample collection, the samples were sorted, the labels checked, caps and seals were checked for leaks and the containers boxed. The soil, Tenax cartridges, carbon cartridges, milk, vegetation, and tissue samples were transferred to frozen storage. Water and sediment samples, which could not be frozen, were refrigerated. Upon return to the laboratory the samples were again frozen or cooled until *analysis*.

6.3.3 Analytical Quality Assurance

Samples were extracted, worked up and analyzed according to the detailed procedures outlined in Appendix A. Throughout the entire procedure, the analysts endeavored to maintain sample integrity and assure accurate analytical results. The salient features of the analytical quality assurance are outlined below.

6.3.3.1 Reagent and Glassware Control

Reagent and glassware control was required in order to minimize contamination. Sample containers, glassware, etc. were cleaned with Isoclean®, rinsed with deionized-distilled water and heat treated at 450-500°C to insure the removal of all traces of organic compounds. Solvents were redistilled in glass in our laboratories prior to their use.

6.3.3.2 Sample Logging

In addition to the field sampling protocol sheets prepared during sample collection, records of analysis progress were maintained. Immediately on return from the field, a log book was established for each sample matrix and each sample logged in. The progress of each sample through the analytical protocol was followed in the sample logbook.

Each instrument operator maintained a detailed log book indicating when the sample was run, the conditions under which it was run, the data which were printed out and the mode of data storage.

6.3.3.3 Instrumentation Control

The performance of each instrument used for sample analysis was evaluated daily by running a standard.

6.3.3.4 Analysis of Quality Control Samples

Quality control samples were interspersed with field samples in the queue for analysis. This protocol was designed to detect contaminants or variations in extraction efficiency with time.

Volatile Brominated Organics.--In addition to the analysis of control samples in Table 6.39, the reproducibility of analysis for volatile brominated organics collected on Tenax GC using GC/MS/COMP (mass fragmentography) was examined on several sets of samples. The results are given in Table 6.40. The first sample of a replicate set was analyzed approximately two and one-half weeks after collection in October of 1976. The second sample from the replicate set was analyzed four months later. The second sample had been kept at -20° during the entire period prior to its analysis. It is evident (Table 6.40) that the reproducibility of analysis ranges from a few percent to ±25%. From these results it was concluded that percent reproducibility for analysis of halogenated hydrocarbons by the technique of high resolution gc/ms/comp was more than adequate for the purpose of this study.

Ethylene.--Validation of sample integrity was achieved through the preparation of eleven vacuum cannisters as blanks or controls. These "quality control" samples, either transported to and from the field with the samples or refrigerated in the laboratory, were prepared to insure (1) that no undetected contamination occurred as a result of transport or storage and (2) that any losses due to leakage from the container or adsorption to the interior of the container be detected. The results of the analysis of these samples were presented in Section 6.0.

The average ethylene concentration found in the blank samples is 0.8 ppm (range 0.1-2.2 ppm). This relatively high blank value is reflected in the results of the control samples, particularly of those spiked at the 0.9 ppm level. Consequently, 0.8 ppm represents the approximate limit of detection for ethylene by this technique. Recovery from control samples containing 9.7 ppm ethylene was significantly closer to that expected. The average recovery at this concentration was 91%.

Decabrom and Tetrabrom.--Soil from the Research Triangle Park was spiked with 100 µg/kg each of Decabrom and Tetrabrom. Analysis by GC/MS/COMP found 110 and 162 µg/kg, respectively. These levels are very near the limit of detection.

Other controls per Table 6.39 were analyzed interdispersed with field samples.

Table 6.40. REPRODUCIBILITY OF REPLICATE MEASUREMENTS FOR HALOGENATED HYDROCARBONS ON TENAX GC SAMPLING CARTRIDGES[a]

Site	Period/Cycle/Location	Allyl bromide	Bromobenzene	Bromoform	1- or 2-Bromo-propane	1-Chloro-3-Bromo-propane	1-Chloro-2,3-Dibromopropane	1,2-Dibromoethane
Great Lakes Corp.	P3/C1/L2	8.4 ± 5.6	20.7 ± 7	15.1 ± 3	10.8 ± 4.4	-	-	1107 ± 32
	P3/C1/L3	-	60 ± 20	11.96 ± 0	-	23.7 ± 4.6	-	1837 ± 162
Ethyl Corp.	P1/C1/L2	-	-	-	-	-	-	174 ± 44
Arkansas Chem. Inc.	P1/C1/L3	29.7 ± 1	-	-	-	-	-	81 ± 15
Michigan Chem. Inc.	P1/C2/L4	32.9 ± 1.5	-	-	35 ± 15	63 ± 6	20.6 ± 5.5	-

[a] The first sample of replicate set was analyzed in October, 1976, the second sample 4 mo. later; all values are in ng/m^3.

6.3.3.5 Data Quality Assessment

The data generated by each analysis were thoroughly examined by the instrument operator to assure quality. In the case of mass spectral data, the data were screened by the instrument supervisor before release. This screen assured data quality and also that the sample had been run according to the request of the analyst.

6.3.3.6 Quality Assurance in Data Interpretation

Both qualitative interpretations and quantitation were spot checked by a second person.

6.4 METHYL CHLORIDE AND METHYL BROMIDE ANALYSIS BY GC/ECD AND MASS FRAGMENTOGRAPHY

6.4.1 Apparatus

Aluminum sample containers were evacuated with a vacuum pump for 15 minutes, flushed with helium, then evacuated again for 15 minutes. They were then checked with a vacuum gauge, and were deemed satisfactory if they showed a vacuum >29".

A stainless steel column (6 ft x 1/8" i.d.) packed with Durapak *n*-octane/Porasil C (100/120 mesh) was used for the analysis. A 1 ml aliquot of each sample was transferred from the container to the column with a 1 ml Pressure-lok® gas syringe (Precision Instrument Corp.). The lower limit of measurement for MeCl and MeBr was 35 ppm and 5 ppm, respectively.

6.4.2 Quality Control

Standards were prepared using the permeation line system. A flow rate was set across the permeation tubes of MeCl and MeBr to create a certain concentration of MeCl and MeBr in N_2. An evacuated aluminum cannister was then attached to a permeation line and allowed to equilibrate with the system, after which the cannister was sealed. Blanks were prepared by filling an evacuated cannister with helium at 1 atm.

The following blanks and controls were prepared:

	Type	Number
Blank	Lab	2
	Field	3
6 ppm MeBr + 35 ppb MeCl	Lab	1
	Field	1
60 ppm MeBr + 350 ppb MeCl	Lab	1
	Field	2
300 ppb MeBr + 1750 ppb MeCl	Lab	1
	Field	1

6.4.3 Analysis of Samples

Standards (Fig. 6.25) to be run each day were prepared on the permeation line, with 1 ml of a standard being drawn directly from the line with a gas syringe. All lab blanks (Fig. 6.26), field blanks, lab controls, and field controls were analyzed. All samples from Dow Chemical were also analyzed.

Blanks contained several large peaks eluting in the general area of MeCl and MeBr, but none that interfered directly with the analysis of the two compounds. None of the controls, however, contained any detectable levels of MeCl and MeBr, indicating that these compounds were not stable in the aluminum cannisters for the period of time stored. Blanks and controls had been stored for 8 to 9 weeks.

Samples from Dow showed no detectable levels of MeBr and MeCl. These samples had been stored for 5 1/2 weeks.

A new control, 900 ppb MeCl and 180 ppb MeBr (Fig. 6.27), was prepared in a cannister exactly as before and analyzed immediately. The appropriate levels of MeCl and MeBr were found. Analysis of this new control five days layer showed approximately a 15% loss of MeCl and MeBr.

No methyl chloride or methyl bromide was detected by mass fragmentography from the analysis of carbon cartridges (Appendix A). Vinyl chloride and vinyl bromide were also not detected.

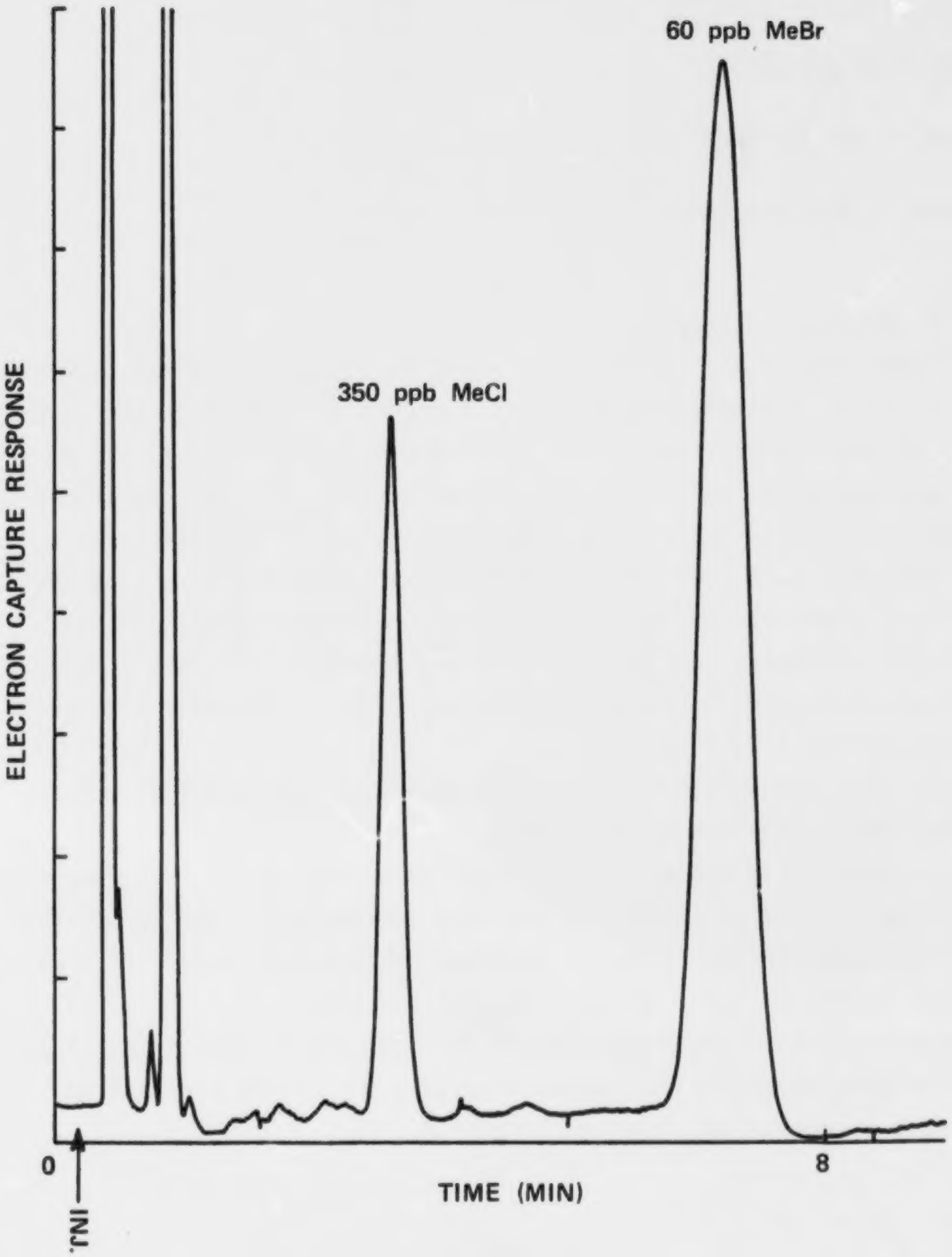


Figure 6.25. GC/ECD of methyl chloride and methyl bromide.

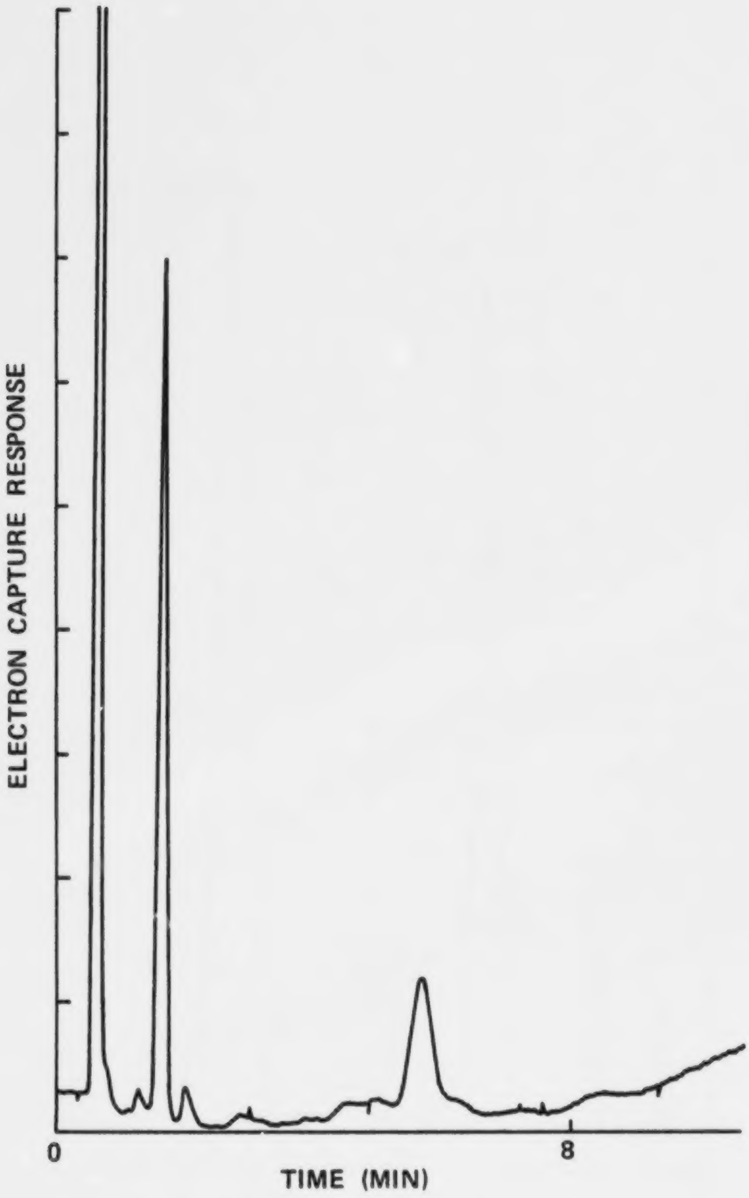


Figure 6.26. GC/ECD of blank control sample.

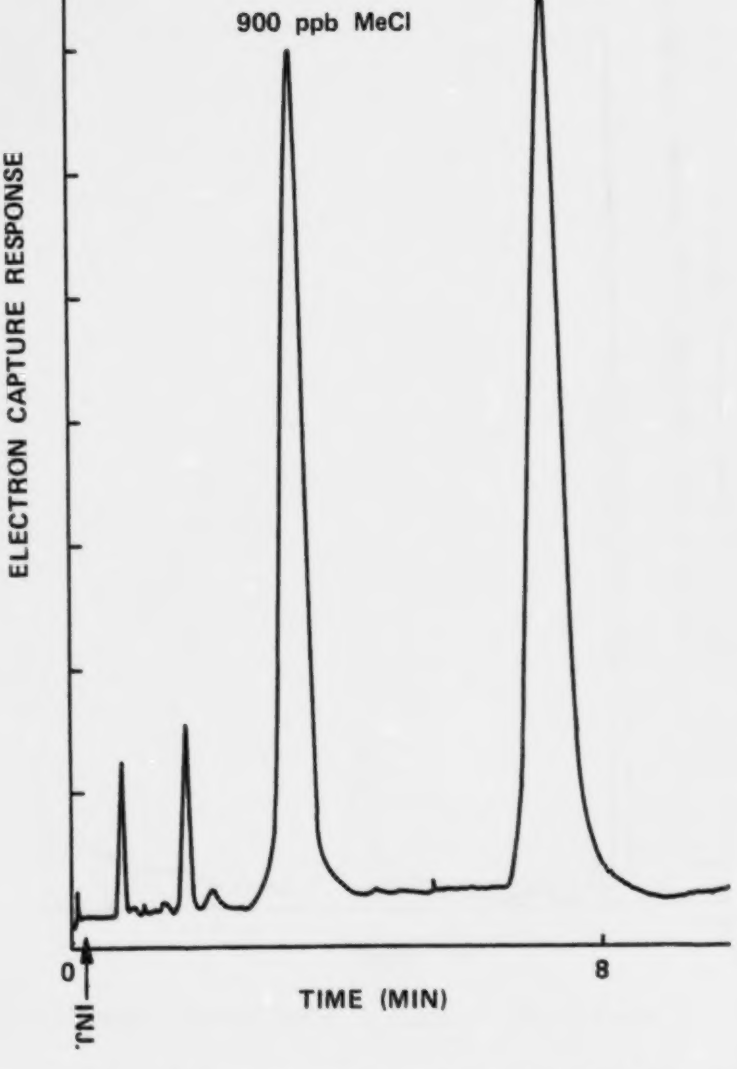


Figure 6.27. GC/ECD of methyl chloride and methyl bromide.